

# **ULTRASONIC AND RELATED STUDIES OF SOLUTIONS**

**A  
THESIS  
SUBMITTED FOR THE DEGREE  
OF**

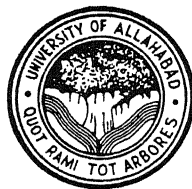
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**IN  
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**PROF. J. D. PANDEY**

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BY  
**NITYA KISHOR SONI**  
*(M. Sc.)*



**DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF ALLAHABAD  
ALLAHABAD**

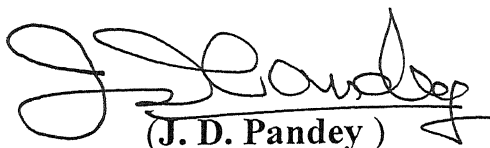
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# CERTIFICATE

This is to certify that **Mr. Nitya Kishor Soni** has fulfilled all the requirements for the submission of the D. Phil. Thesis entitled **“ULTRASONIC AND RELATED STUDIES OF SOLUTIONS”** to the University of Allahabad. This is the record of candidate's own effort under my guidance and supervision.

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Date : 25<sup>th</sup> June 2002



(J. D. Pandey )

D. Sc.

Former Head  
(Supervisor)

Department of Chemistry  
University of Allahabad  
Allahabad 211 002, India

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N. K Soni

**Nitya Kishor Soni**

## PREFACE

Ultrasonic studies has been found to be the most powerful tool for the structural and interaction studies of liquids and liquids solutions. A number of thermodynamic properties of liquids and liquid solutions can be estimated directly from the knowledge of ultrasonic velocity and density data. In the present thesis an attempt has been made to carry out the experimental measurement of ultrasonic velocity, density and refractive index of binary and ternary solutions containing ethanol (polar) and n-alkanes (non-polar) components at 308.15K and different compositions.

The properties of multicomponent solutions containing alcohol with n-alkanes are of interest in the technology of alcohol-blended-gasoline. These are also used in the reformulation of gasoline, to improve octanerating and pollution reducing capability of gasoline.

Some other properties viz. surface tension and viscosity has also been evaluated theoretically.



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# **CHAPTER I**

## **Introduction**

The composition dependence of thermodynamic properties of binary liquid solutions has been proved to be an useful tool in elucidating the structural interactions among the components<sup>1-5</sup>. A lot of attention has been focussed on the theoretical and experimental investigation of the excess thermodynamic properties nonelectrolyte solutions in recent years. If we know the properties of a pair of pure components, we can make a theoretical treatment of what happens when they are mixed to form a solution.

Multicomponent liquid systems, rather than single component, are widely used in processing and product formulations in many industrial applications. In chemical industry, knowledge of the physical and thermodynamic properties of multicomponent systems is essential for design calculations involving separation, fluid flow, mass transfer and heat transfer. Thermodynamic and transport properties of liquid solutions have been used to study the departure of a real liquid solution from ideality as well as to study the intermolecular interactions between various species present in the solution. The properties of multicomponent liquid solutions containing alcohol and two or more n-alkanes are of interest in the technology of alcohol-blended-gasoline. Mixtures containing oxygenated compounds, such as ether or alkanols (-OH group), are of great importance from a practical point of view due to their octane enhancing and pollution reducing properties. When two liquids are mixed, the resulting change in physical and thermodynamic properties may be considered as the sum of several contributions due to change in combinatorial, energetic, free volume and molecular orientation order due to steric hinderance. If either of the liquid or both are polar molecules, order destruction or order creation upon mixing gives rise to additional contributions, which have opposite sign in thermodynamic properties. Systematic studies of multicomponent liquid systems containing organic liquid as component molecules started as early as 1980<sup>6-12</sup>.

Ultrasonic techniques has been found to be the most powerful tool for the structural and interaction studies of liquid and liquid systems. A number of thermodynamic properties of liquid systems can be estimated directly from the knowledge of ultrasonic velocity and density data. Ultrasonic propagation assumes:

(i) no loss in fluid and (ii) adiabatic nature of the process. The study of ultrasonic propagation has indicated that both the thermodynamic treatment and that of relaxation processes furnish for the ultrasonic velocity in the limit of low frequencies.

Sound velocity has been used to test various theories<sup>13-15</sup> (Free volume theory, Scaled particle theory, Significant structure theory, Flory theory and Hard sphere theory) for simple pure liquids. It has also been applied to few binary solutions.

Ultrasonic velocity has now been accepted as an important tool to study molecular interactions, structural and physicochemical behaviour of liquids and liquid mixtures. A number of useful and important thermodynamic properties of a liquid system can be evaluated with the help of an ultrasonic velocity and density data. Very accurate and precise measurement of ultrasonic velocity and density can be made using comparatively low cost instrument. Extensive work has been done and also is in progress on the measurement of ultrasonic velocity and density in binary liquid solutions. These data are employed to deduce a number of useful thermodynamic properties and study of molecular interactions through excess functions obtained from ultrasonic velocity and density data. There are numerous papers and it is not possible to mention all. However, some recent investigations<sup>22-30</sup> are cited. Ultrasonic velocity and density measurements in multicomponent liquid mixtures have gained momentum during recent years<sup>31-36</sup>.

Some more useful properties of liquid mixtures which are not easily accessible (such as isentropic compressibility) by other means, can be calculated using ultrasonic velocity and density data. Isentropic compressibility is a key parameter in the liquid state theory. We know that density of liquid solutions and related volumetric properties are required for many applicative aspects, as well as for theoretical calculations. Particularly, their knowledge is indispensable when the classical and thermodynamic approach is to be used to relate and to compute the equilibrium properties of mixtures. From this point of view, they are of strategically important for both the test of existing theories and the developments of new models for mixture behaviour. For practical purposes, (tank design, pipe-lines etc.) the knowledge of volume of liquid mixtures is more important than the corresponding density value. Various thermodynamic and transport properties depends upon the precision of

density measurements. It is well recognized that ultrasonic velocity, molar volume and isentropic compressibility of liquid mixtures provide information on the molecular interactions. The high precision of speed of sound measurement makes it possible to calculate reliable values of the parameters characterizing deviations of the liquid systems from ideality, the excess isentropic compressibility  $K_s^E$ , which proves to be one of the most reproducible of the excess properties and deviation of speed of sound  $\Delta u$ , from those in ideal mixtures. Molecular association in solution and some important correlation with various parameters e.g. ratio of the heat capacity  $\gamma$ , isentropic and isothermal compressibilities  $K_s$  and  $K_T$ , deviation in isentropic compressibility  $\Delta K_s$ , can be very well studied through speed of sound measurements in liquid mixtures.

In recent years there has been an increased interest in the determination of either isothermal compressibility or isentropic compressibility. The role that isentropic compressibility plays in the thermodynamic characterization of binary liquid mixtures is also subject of recent years<sup>37</sup>. The isentropic compressibility may be used to separate the contribution of pressure and temperature in the change of thermodynamic properties measured along the saturation curve. Isentropic compressibility and ultrasonic velocity will be the basic experimental thermodynamic properties in the present investigation.

Several workers have pointed out that excess thermodynamic functions are sensitively dependent not only on the differences in molecular forces, but also on the difference in the size of the molecules. It is obvious that the study of excess compressibilities and excess volumes gives important information on the intermolecular forces determining the properties of liquid mixtures. Interaction between component molecules can be investigated from speed of sound and density data using statistical theory of solutions. Excess thermodynamic functions ( $V^E$ ,  $K_s^E$ ,  $\Delta n$  and  $\Delta R_m$ ) have been used as a qualitative and quantitative guide to predict the extent of complex formation in binary liquid mixtures. There has been considerable interest<sup>38-46</sup> in the theoretical and experimental investigation of the excess thermodynamic properties of liquid solutions.

Excess volume plays very important role in structural and interaction studies of multicomponent systems. It is observed that  $V^E$  of two liquids can arise from any one or both of the following factors like difference in size and shape of the component molecules, structural changes such as change in correlation of molecular orientation, difference in the molecular interactions, formation of new chemical species through hydrogen bonding or electron donor acceptor interactions and distribution of existing dipolar order or hydrogen bonding.

Ultrasonic velocity data when coupled with molar volume, thermal expansion coefficient, and heat capacity, provide information about a number of thermodynamic parameter of liquid solutions. These parameters can further be used to study the structural changes and molecular interactions. Several approaches are found in literature<sup>47-54</sup> to estimate excess compressibility ( $K_s^E$ ). The term excess compressibility has been used to denote several thermodynamically different quantities and more precisely it refers to the deviation of the compressibility of the solutions from that of an ideal solution.

Significant amount of experimental and theoretical work on  $V^E$  and  $K_s^E$  of multicomponent liquid systems has been done during recent years<sup>55-62</sup>. While studying the thermodynamic properties of mixtures, refractive index cannot be neglected. In a number of applications of multiphase systems, knowledge of refractive indices is desirable. The knowledge of refractive index and molar refraction is useful for predicting many physicochemical properties of liquid mixtures. Refractive index is used to evaluate the molar refraction and molecular connectivity which are used in predicting the structure of the liquids and liquid mixtures. From time to time several empirical and semi-empirical mixing rules for predicting the refractive index of binary and ternary liquid mixtures have been proposed. The validity of various mixing rules as proposed by Lorentz-lorenz, Gladstone-Dale, Wiener, Arago-Biot, Heller, Eykman and Oster have been tested by various workers during recent years<sup>63-66</sup>. The literature survey reveals that limited studies were made on the experimental measurements of refractive index in multicomponent systems. However, significant amount of experimental and theoretical work on refractive index of liquid mixtures has been done during recent years<sup>67-74</sup>.

The knowledge of the solution properties for solution of two, or more components is frequently required in the understanding of the transport phenomena as well as in the industrial chemical processes. During recent years, the mixture of binary nonelectrolyte liquids have been studied from different angles e.g. from the view point of existence of specific interactions leading to the formation of intermolecular adducts between the components in the liquids state, as well as other type of interactions occurring in such solutions. Equilibrium and thermodynamic properties are studied widely for a number of mixtures and statistical theories are developed to correlate these properties with intermolecular forces. But the study of transport properties is equally informative and can give an insight into the intermolecular forces and microscopic structure of liquids. Viscosity, one of the transport properties, has most widely used to study molecular interactions and physicochemical behaviour of liquid mixtures. During recent past, a number of papers<sup>75-83</sup> are appearing on the experimental studies of binary liquid mixtures. However, few multicomponent liquid systems<sup>84</sup> were also studied using viscosity data. Comparatively less attention is given on the theoretical investigation of viscosity for liquid mixtures. Various empirical and semi-empirical relations (Frenkel<sup>85</sup>, Kendall-Munroe<sup>86</sup>, Additive<sup>87,88</sup>, Bingham<sup>89</sup>, Katti-Chaudhari<sup>90</sup>, Grunberg-Nissan<sup>91</sup> and Hind-McUbbelhode<sup>92</sup>) connecting viscosity and mole fraction of binary liquid mixtures have been proposed and tested by various workers. These relations are further extended to multicomponent systems<sup>93-95</sup>.

The most widely accepted Flory's statistical theory has been applied to binary liquid mixtures by Bloomfield and Dewan<sup>96</sup>. Further rectification was done by Delmas<sup>97</sup> and Turel. In a series of papers Pandey et al<sup>98-100</sup> extended Flory's statistical theory to study the viscous flow mechanism in multicomponent systems. Theoretical evaluation of viscosity of binary liquid mixtures has also been made on the basis of Significant Structure Theory developed by Eyring et al<sup>101,102</sup>. This theory has been further employed to predict viscosity of multicomponent liquid systems<sup>97,103</sup>. Recently Rasmussen et al<sup>94</sup> used statistical thermodynamic approach through partition function to obtain expression for dynamic viscosity of liquid solutions, and the resulting equation is tested for a large number of binary liquid solutions and few

multicomponent solutions. Viscosity of multicomponent solutions has also been theoretically evaluated from the values of their contributory binaries using the approach developed by Acree et al (BAB) for estimating the thermodynamic properties of multicomponent systems<sup>104-107</sup>. In 1981, Pandey et al<sup>108</sup> applied Sutherland Wassiljewa relation<sup>109</sup> based on the theory of mean free path, for computing the viscosity of multicomponent gas mixtures. In the present work we have tried to present a completely different approach to the problem of viscosity of multicomponent liquid mixtures. For the first time, to the best of our knowledge, the Sutherland-Wassiljewa relation has been applied to compute the viscosity of multicomponent liquid systems. This equation has been found to be very versatile since it is able to predict the maxima and minima in the viscosity versus composition curve in the case of binary liquid mixtures, which was not predicted by earlier viscosity relations<sup>110</sup>. This approach has been applied in the present context on a wide spectrum of binary and multicomponent systems. The results are found to be quite encouraging as evidenced from the results of calculation. Moreover, for computing the viscosity of mixtures only the experimental values of viscosity and molecular weight of pure components along with the two adjustable parameters  $A_{ij}$  and  $A_{ji}$  are required. These parameters called Wassiljewa coefficients in the molecular theory of gases and physical significance has been very recently discussed<sup>111</sup>.

Successful attempts have been made by several workers<sup>112-115</sup> to calculate theoretically the surface tension of liquid solutions. Among all the methods known, so far, the most sophisticated are: (i) Flory theory extended for binary liquid mixtures and (ii) the refined version of Average Potential Model of Prigogine<sup>116,117</sup>. In the year 1977, a comparative study of the surface tension values obtained from APM and Flory theory has been done for few binary liquid mixtures. Brock and Bird<sup>118</sup> correlated the surface tension data of liquids and metals with the modified form of principle of corresponding state and derived surface tension models in terms of critical constants. This equation was further extended to binary<sup>112</sup> and multicomponent<sup>119</sup> liquid systems. In the year 1983, Pandey and Pant<sup>120</sup> formulated the Flory Patterson theory for estimating the surface tension of ternary polymeric liquid mixtures. A number of other theories viz. volume fraction statistics<sup>121</sup> and Sanchez<sup>122</sup> method etc were



applied to multicomponent liquid solutions during recent years in addition to Flory theory and Brock-Bird relation. For nonelectrolyte solutions, sound velocity has also been correlated with surface tension<sup>119</sup>. In the year 1994, surface tension of ternary liquid mixtures  $N_2+O_2+Ar$  has been measured<sup>123</sup> accurately at different temperatures and varying pressures. In our knowledge this is the first kind of measurements available in the literature. Purpose of the present work is to analyze the experimental data of surface tension of ternary solution  $N_2+O_2+Ar$  reported using Brock-Bird method. In this case no other theoretical methods can be applied due to scarcity of data needed. Similarly, an attempt has been made to evaluate the excess surface tension of number of equimolar binary solutions at different temperatures and varying pressures using the methods developed by Rowlinson<sup>124</sup> and Guggenheim<sup>125</sup>.

The objectives of present work are as follows:

1. To study the effect of size, shape and polarity of the component molecules on the excess thermodynamic functions.
2. To obtain accurate experimental data on various physico-chemical properties such as density, ultrasonic velocity and refractive index for binary and ternary solutions containing polar and non-polar components at different composition.
3. To derive various excess thermodynamic functions for the individual properties from the measured data of pure and mixtures.
4. To examine the sensitivity of the composition dependence of the variety of thermodynamic properties in order to understand the nature and extent of molecular interactions.
5. To test the various existing theories of solution based on statistical methods with the experimentally derived properties.

The present thesis entitled “**Ultrasonic and related studies of solutions**” has been divided into eight chapters. The experimental investigation consist of the experimental measurements and the interpretations of thermodynamic, ultrasonic and transport properties of liquid solutions. To achieve this goal two binary systems namely ethanol+hexane; ethanol+dodecane and one ternary system

ethanol+hexane+decane were taken and the measurements were carried out at 308.15K.

The first chapter of the thesis entitled “Introduction” provides an insight of the aim of the investigation in terms of the experimentally determined and computed parameters. An upto date literature survey has been presented to illustrate the work being carried out in this field.

“Experimental techniques” which are being used in the present investigation is the title of the second chapter. This chapter deals with the experimental techniques, which have been employed for the measurement of ultrasonic velocity, density and refractive index.

The third chapter of the thesis entitled “Experimental values of ultrasonic velocity, density and refractive index for binary and ternary solutions” records all the three properties ( $u$ ,  $\rho$  and  $n$ ) determined precisely for the systems under the present investigation.

The fourth chapter gives computed values of excess volume, ( $V^E$ ), excess isentropic compressibility ( $K_s^E$ ) and deviation in isentropic compressibility ( $\Delta K_s$ ) for the binary liquid mixtures evaluated from the ultrasonic velocity and density of respective liquid solutions.

The aim of chapter five is the evaluation of change in refractive indices ( $\Delta n$ ) and change in molar refraction ( $\Delta R_m$ ) for two binary and one ternary systems under investigation. Refractive index values for all the systems have been determined theoretically by employing various empirical and semi-empirical relations and then compared with the experimental values in terms of average percentage deviation (APD).

Chapter six deals with the theoretical evaluation of viscosity by making use of Sutherland-Wassiljewa equation for the systems under investigation. The values obtained have then been compared with the literature values.

Chapter seven of the thesis deals with the computation of surface tension of ternary liquid mixtures with a modified Brock-Bird relation at varying temperatures and pressures. The computations have been carried out for various compositions at temperature ranging from 90 to 110 K and vapour pressure upto 865 kPa.

The aim of concluding chapter is evaluation of excess surface tension of some binary mixtures at varying temperatures and pressures. The values of excess surface tension obtained are compared with the values obtained using the Guggenheim relation to estimate the surface tension of the mixtures.

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## **CHAPTER II**

# **Experimental techniques for the measurement of density, ultrasonic velocity and refractive index**

The experimental techniques used for the measurement of density ( $\rho$ ), ultrasonic velocity ( $u$ ) and refractive index ( $n$ ) have been divided into following parts :

### **(1) Temperature control:**

All the measurements have been carried out in a thermostatic bath in order to maintain a uniform and constant temperature. The over all precision in the temperature was found to be  $\pm 0.05$  °C.

### **(2) Liquids used for the calibration :**

The liquids used for the calibration are triple distilled water, ethanol (B. Chemicals), decane (s. d. fine-chem. Ltd.), dodecane (Wilson laboratory), hexane (E. Merck) and DMF (E. Merck). These liquids were further purified to ensure their purity by the usual methods.

### **(3) Calibration and measurement:**

#### **Calibration of pycnometer and density measurement**

Densities of pure liquids and their mixtures were measured using a single-stem pycnometer (made of pyrex glass having a bulb of  $8 \times 10^{-6}$  m<sup>3</sup> and capillary with graduated marks, and a uniform bore of  $1 \times 10^{-3}$  m which could be closed by using a well fitting glass cap) as described by Nath<sup>1</sup>.

The total volume of pycnometer and the marks on the capillary were calibrated by using triple distilled water at 308.15 K in the following manner:

First we take the weight of empty pycnometer ( $w_1$ ) using a K. Roy balance (Model No. K-15 super with a precision of  $\pm 1 \times 10^{-4}$  g) and transfer the water into it. The liquid inside the capillary is removed using fine strips of Whatmann filter paper. The pycnometer is kept for about 25 min (when liquid level attains stationary state) in a water bath and the position of liquid level is noted. Now, weight of the pycnometer containing liquid is again determined ( $w_2$ ). The difference of these two weights ( $w_2 - w_1$ ) gives the mass of liquid in pycnometer.

From the knowledge of mass and density of water at 308.15 K we can calculate the volume of a liquid at that particular level or mark as

$$\text{Volume} = \text{Mass/Density}$$

where the value of density is taken from the literature<sup>2</sup>

Now, we find out the volume of water at two different levels (marks) as mentioned above and count the number of divisions between these two marks on capillary, we calibrate the volume of one division on capillary as

$$\text{Volume of one division} = \Delta V/n$$

where,  $\Delta V$  is the difference in the volume between two different marks and  $n$  the number of divisions between the two different marks. Thus by knowing the volume and mass of the liquid we can measure the density of the liquid using the relation

$$\rho = \frac{M}{V}$$

The overall experimental uncertainty in the density measurement was estimated to be  $\pm 0.0001$  g/cc.

**Table - 1**

**Measured values of densities of pure liquids along with the literature values at 308.15 K**

Pure liquids	Experimental value of density ( $\rho$ ) ( $\text{kg m}^{-3}$ )	Literature value of density ( $\rho$ )( $\text{kg m}^{-3}$ )
Water	994.1	994.1 [Ref.2]
Ethanol	777.5	777.06 [Ref.3]
Decane	717.8	718.2 [Ref.4]
Dodecane	737.2	738.1 [Ref.4]
DMF	935.8	935.7 [Ref.3]
Hexane	645.8	644.7 [Ref.4] 645.6 [Ref.5]

## Calibration and measurement of ultrasonic velocity:

Ultrasonic velocity ( $u$ ) in pure liquids and their mixtures were measured using an ultrasonic interferometer supplied by M/s Mittal Enterprises, New Delhi, operating at frequency of 2 MHz. The details of the ultrasonic interferometer have been described by other workers.<sup>5-11</sup>

An ultrasonic interferometer consist of the following parts:

### (1) High frequency generator

(2) **Double walled measuring cell:** Containing experimental sample at a constant temperature.

(3) **Micrometer:** For reading the distance travelled by the micrometer between two successive maxima.

**Principle:** The determination of velocity is based on the accurate determination of the wavelength ( $\lambda$ ) in the medium.

### Determination of wavelength ( $\lambda$ ):

Ultrasonic waves of known frequency ( $\nu$ ) are produced by a quartz plate fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz plate. If the separation between these two plates is exactly whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to a reaction on the generator driving the quartz plate and the anode current of the generator becomes maximum. If, now the distance is decreased or increased and variation is exactly one half of the wavelength or multiple of it, anode current again becomes maximum.

The distance travelled by micrometer between two successive maxima is just half of the wavelength, and for each set of reading 'd' for two maxima were recorded. This distance gives the value of wavelength ( $\lambda$ ) as

$$d = n \cdot \lambda / 2$$

where 'n' is the number of maxima and d the distance travelled by micrometer in n number of maxima (in mm). Thus from the knowledge of wavelength ( $\lambda$ ) and frequency ( $\nu$ ), the ultrasonic velocity (u) can be obtained by the relation

$$u = \nu \lambda$$

$$\lambda = 2 \cdot d \text{ (in mm)} / n = 2 \times 10^{-3} d \text{ (in m)} / n \quad \text{and} \quad \nu = 2 \text{ MHz} = 2 \times 10^6 \text{ Hz}$$

The working of the interferometer was tested by making measurements in number of pure liquids.

**Table - 2**  
**The measured values of ultrasonic velocity in pure liquids**  
**along with the literature values at 308.15 K**

Pure liquids	Experimental values ( $\text{ms}^{-1}$ )	Literature values ( $\text{ms}^{-1}$ )
Water	1518.00	---
Ethanol	1118.57	1117 [Ref.5]
Decane	1194.00	1195.56 [Ref. 13]
Dodecane	1234.00	---
Hexane	1034.85	1034 [Ref. 14] 1032.4 [Ref. 15]
Cyclohexane	1208.00	1212.0 [Ref.12]
DMF	1432.50	1428.5 [Ref.5]

## **Adjustment of ultrasonic interferometer:**

The following steps are followed for the adjustment of ultrasonic interferometer:

- (1) The metal base of the measuring cell is connected with the frequency generator with the help of coaxial cable provided with the instrument.
- (2) The clean and dry container of the measuring cell is filled with the experimental sample. It is then fitted with the reflector component.
- (3) The container of the cell is placed in the square base socket and is clamped tightly by a screw provided on the one side of the base.
- (4) The generator is switched on and left for a few minutes for stable working so as to produce standing waves in the liquid.
- (5) The position of the pointer of the micro ammeter is adjusted with knob marked as adjustment and the knob marked again is used to increase the sensitivity of the instrument for generator deflection if necessary.

## **Precautions:**

- (1) The generator was always switched on after filling experimental sample in the cell.
- (2) After the measurement, the experimental sample was taken out and cell was kept clean and dry.
- (3) The micrometer was kept open at 25 mm after use.



### **Refractive index measurement:**

A number of workers<sup>16-24</sup> have measured refractive index of liquids and liquid solutions using Abbe refractometer.

Here, the refractive index of liquids and their solutions was measured directly with calibrated and thermostated instrument called Abbe refractometer at wavelength of the D-line of sodium, 589.3 nm. The instrument was calibrated from time to time with the help of a glass of piece of known refractive index ( $n = 1.1519$ ) provided with the instrument. It was also calibrated using triple distilled water, toluene, decane and ethanol at known temperature.

### **Calibration and mode of operation of Abbe refractometer:**

A thin film of liquid (known refractive index) is placed between the two prisms P, P' (made of glass having relatively high refractive index). Light from a suitable source of light e.g. sodium lamp is made to fall on to the lower part of the lower prism with the help of mirror (M). The position of prism box is adjusted with the help of a side knob so that the sharp edge of the light band in the field of view of the telescope is seen to coincide with the crosswire, at this position the reading on the scale gives the value of refractive index of the liquid and this value of refractive index must be equal to the literature value of the liquid used. If it is not so, then we adjust the side knob so that its scale reads refractive index equal to literature value of liquid and then move the screw attached to telescope in such a manner that the sharp edge of the light band in the field of view of the telescope is seen to coincide with the crosswire in the telescope. Thus, the calibration of instrument is completed. Now we

check the calibration of the instrument by measuring the refractive index of various liquids of known refractive index.

Since the instrument is calibrated in terms of refractive index values, a direct reading on scale gives the refractive index of the liquids and liquid solutions.

**Precaution:** Prisms are cleaned with acetone and dried after each reading.

### **Brief description of Abbe refractometer:**

- (1) It has water jacketed prism box : allows measurement of refractive index at the desired temperature.
- (2) Measurable range extends from 1.300 to 1.700.
- (3) Accuracy 0.001 by direct reading and 0.0001 by estimation.
- (4) Finely marked glass translucent arc scale.
- (5) It permits the measurement of percentage of sugar.

**Table - 3**

**The measured values of refractive index (n) of pure liquids  
along with literature values at different temperatures.**

S.No.	Pure component	T (K)	Experimental value	Literature value
1.	Water	303.15	1.4913	----
2.	Decane	303.15	1.4082	----
3.	Decane	308.15	1.407	1.4081[Ref 24]
4.	Ethanol	303.15	1.360	
5.	Ethanol	308.15	1.357	----
6.	Hexane	308.15	1.372	1.36626 [Ref.14 & 23] 1.3681[Ref 24]
7.	Dodecane	308.15	1.417	----

## Preparation of Samples:

All binary solutions viz. ethanol+hexane; ethanol+dodecane; and ternary solution namely ethanol+hexane+decane were prepared by weighing. The ternary solutions (mole fraction,  $x_i$ ) were obtained by adding a pure component (ethanol) to a stock solution of binary mixture of other components (hexane+decane). Thus this ternary mixture can be treated as a pseudobinary mixture.

## Calculation for composition (mole fractions) determination in ternary mixture:

Firstly, we find out the weight fraction of any component in stock solution of binary mixture of hexane+decane,

Weight fraction of hexane = Wt. of hexane / total weight of stock soln.  
(hexane+decane)

It is the weight of hexane in 1 g of stock solution of hexane+decane.

Now we take a certain volume of stock solution and add a certain volume of III<sup>rd</sup> component (ethanol) to prepare a ternary solution.

If we take  $V_{(\text{stock})}$  ml of stock solution and  $V_{(\text{eth})}$  ml of ethanol to prepare the ternary mixture then composition of the ternary mixture can be calculated as,

I<sup>st</sup> : Weight of hexane in  $V_{(\text{stock})}$  ml = weight fraction of hexane  $\times$  weight of  $V_{(\text{stock})}$  ml

II<sup>nd</sup> : Weight of decane in  $V_{(\text{stock})}$  ml = weight of  $V_{(\text{stock})}$  ml of stock solution - weight of hexane in  $V_{(\text{stock})}$  ml of stock solution

III<sup>rd</sup>: weight of ethanol in ternary mixture - weight of stock solution

Thus, by knowing the weight of each component in ternary mixture we can find the mole fraction of each component using the formula

No. of mole of any component ( $n_i$ ) = Mass of  $i^{\text{th}}$  component / Molecular weight of  $i^{\text{th}}$  component.

Now,

Mole fraction of component ( $x_1$ ) in ternary mixture =  $n_1 / n_1 + n_2 + n_3$

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## **CHAPTER III**

**Experimental values of density,  
ultrasonic velocity and refractive  
index of binary and ternary  
solutions**



## Introduction

The measurement of density, ultrasonic velocity and refractive index of liquid solutions is found to be an important tool in knowing the physicochemical behaviour of systems. These properties have been used to obtain a number of thermodynamic parameters which are utilised to study the intermolecular interactions in liquid mixtures. Several workers<sup>1-21</sup> have reported the density ( $\rho$ ), ultrasonic velocity ( $u$ ) and refractive index ( $n$ ) values of binary liquid mixtures. The thermodynamic properties of binary liquid mixtures, containing a simple hydrocarbon as one of the component, have received considerable interest during recent years<sup>22, 23</sup>. The interest arise because of the fact that the mixing behaviour of the binary mixtures of type A+B is highly dependent upon the geometry, size and structure of both the components<sup>24</sup>. The molecular interactions of either structure breaking or structure forming type are possible depending upon the type of components. Extensive work has been done and still in progress on experimental determination of these properties of binary liquid mixtures<sup>25, 26</sup>.

The present chapter reports the experimental values of density, ultrasonic velocity and refractive index of two binary solutions viz. ethanol+hexane; ethanol+dodecane and one ternary solution namely ethanol+hexane+decane.

## Experimental

All the organic liquids used were of AR grade obtained from standard companies and further distilled to ensure their purity. All the measurements were made at 308.15 K. The complete details of the experimental measurements of density ( $\rho$ ), ultrasonic velocity ( $u$ ) and refractive index ( $n$ ) have described in previous chapter.

## Results and discussion

The experimental values of density ( $\rho$ ), ultrasonic velocity ( $u$ ) and refractive index ( $n$ ) for pure components, binary liquid solutions namely ethanol+hexane; ethanol+dodecane and ternary liquid solution viz. ethanol+hexane+decane are reported in tables 1, 2, 3 and 4 respectively.

A close perusal of table 2 shows that in system ethanol+hexane as the concentration of ethanol increases (concentration of hexane decreases) the density ( $\rho$ ) and ultrasonic velocity ( $u$ ) both increases whereas refractive index values decrease. In system ethanol + dodecane (table 3), refractive index ( $n$ ) and ultrasonic velocity, decreases whereas the density of the mixture increases with increase in concentration of ethanol (decrease in concentration of dodecane).

In ternary system, ethanol( $x_1$ ) + hexane( $x_2$ ) + decane( $x_3$ ) (table 4), in which the ratio of  $x_2 / x_3$  remains constant (0.3528) over entire composition range while  $x_1$  is variable, the ultrasonic velocity and refractive index values decrease while density of the mixture increases with increase in value of  $x_1$ .

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**Table - 1**

**Experimental values of density ( $\rho$ ), ultrasonic velocity ( $u$ )  
and refractive index ( $n$ ) of pure components at 308.15 K**

<b>Component</b>	<b>Mol. Wt.</b>	<b><math>\rho</math> (kg m<sup>-3</sup>)</b>	<b><math>u</math> (m s<sup>-1</sup>)</b>	<b><math>n</math></b>
Ethanol	46.07	777.50	1118.57	1.357
Hexane	86.18	645.80	1034.85	1.372
Decane	142.28	717.80	1194.00	1.407
Dodecane	170.34	737.20	1234.00	1.417

**Table - 2**  
**Experimental values of density ( $\rho$ ), ultrasonic velocity ( $u$ )**  
**and refractive index ( $n$ ) of binary solution ethanol ( $x_1$ ) +**  
**hexane ( $x_2$ ) at 308.15 K**

Mole fraction ( $x_1$ )	$\rho$ (kg m <sup>-3</sup> )	$u$ (m s <sup>-1</sup> )	$n$
0.0486	655.2	1006.79	1.371
0.1529	661.5	1009.24	1.370
0.3512	675.9	1021.42	1.367
0.5001	690.0	1032.16	1.364
0.6472	708.5	1044.61	1.362
0.7996	734.1	1065.05	1.359
0.9469	766.3	1102.10	1.357

**Table - 3**  
**Experimental values of density ( $\rho$ ), ultrasonic velocity ( $u$ )**  
**and refractive index ( $n$ ) of binary solution ethanol ( $x_1$ ) +**  
**dodecane ( $x_2$ ) at 308.15 K**

Mole fraction ( $x_1$ )	$\rho$ (kg m <sup>-3</sup> )	$u$ (m s <sup>-1</sup> )	$n$
0.2989	740.4	1185.83	1.4145
0.4002	741.9	1167.59	1.4083
0.5001	743.7	1156.25	1.3945
0.5488	744.8	1152.39	1.3855
0.6001	746.2	1148.08	1.3750
0.6996	750.1	1143.37	1.3551
0.8001	756.0	1137.41	1.3429
0.9002	764.5	1130.04	1.3508
0.9502	770.1	1124.85	1.3670

**Table - 4**

**Experimental values of density ( $\rho$ ), ultrasonic velocity ( $u$ )  
and refractive index ( $n$ ) of ternary liquid solution ethanol  
( $x_1$ ) + hexane ( $x_2$ ) + decane ( $x_3$ ) at 308.15 K**

Mole fraction ( $x_1$ )	Mole fraction ( $x_2$ )	$\rho$ ( $\text{kg m}^{-3}$ )	$u$ ( $\text{m s}^{-1}$ )	$n$
0.0492	0.2480	706.8	1158.66	1.402
0.1826	0.2132	711.2	1155.14	1.400
0.3298	0.1748	714.5	1141.14	1.398
0.4715	0.1378	719.8	1138.46	1.395
0.6265	0.0974	730.4	1120.00	1.385
0.7175	0.0737	741.8	1116.00	1.377
0.9441	0.0146	768.1	1097.71	1.364



## **CHAPTER IV**

**Excess volume, deviation in  
isentropic compressibility and  
excess isentropic compressibility  
of binary solutions**

## Introduction

The excess thermodynamic functions, which depend on the temperature, pressure and composition of the system, have a great significance in chemical engineering in the design of industrial separation process. The abrupt departure from ideal behaviour of some physical properties like volume, compressibility etc. helps in studying the interaction between the molecules. Excess volume ( $V^E$ ) is a fundamental thermodynamic property because the knowledge of the mixing volume effects are very useful for a number of practical applications like paints, varnishes, painting ink etc.

Measurements of excess molar volume ( $V^E$ ) are now made with either continuous dilution dilatometer<sup>1-3</sup> or with single capillary pycnometer<sup>4-6</sup> or commercially available digital densimeter<sup>7, 8</sup>. It is well known<sup>9</sup> that sign and magnitude of excess volume gives information about the strength of interactions between unlike molecules in the binary mixtures. The large positive values of  $V^E$  indicate weak interactions while large negative values of  $V^E$  indicate strong interactions, and intermolecular association i.e. formation of complex.

Like excess molar volume ( $V^E$ ), excess isentropic compressibility ( $K_s^E$ ) of liquid mixtures also provides information about molecular interactions. The high precision in the measurement of speed of sound ( $u$ ) and density ( $\rho$ ) makes it possible to calculate reliable values of this property characterizing deviation of the system from ideality. The excess isentropic compressibility plays an important role in thermodynamic characterization of binary liquid mixtures. It has also been pointed out by numerous workers<sup>1-12</sup> that thermodynamic functions are very sensitive and depend not only on the difference in intermolecular interactions but also on the difference in the size of the molecules. Experimental measurements of excess volume and isentropic compressibility of multicomponent liquid mixtures have been carried out by various workers<sup>1-12</sup> during recent years.

In the present chapter an attempt has been made to determine excess volume ( $V^E$ ), deviation in isentropic compressibility ( $\Delta K_s$ ) and excess isentropic compressibility ( $K_s^E$ ) for two binary liquid solutions, viz. ethanol+hexane and ethanol+dodecane and for one ternary liquid system namely ethanol+hexane+decane

308.15 K. The experimental values of ultrasonic velocity ( $u$ ) and density ( $\rho$ ) are reported in earlier chapter.

### Method of estimation of $V^E$ , $K_s^E$ and $\Delta K_s$ :

The excess molar volume ( $V^E$ ) is calculated from the density measurement using the relation

$$V^E = V_m - V_{id} \quad (1)$$

where  $V_{id}$  is the ideal molar volume and  $V_m$  is the molar volume of the mixture. The molar volume of the mixture is given by

$$V_m = \sum x_i M_i / \rho_m \quad (2)$$

where  $x_i$  and  $M_i$  are the mole fraction and molecular weight of  $i^{\text{th}}$  component in the mixture respectively, and  $\rho_m$  is the measured value of the density of mixture. Ideal molar volume ( $V_{id}$ ) is obtained from,

$$V_{id} = \sum x_i V_i \quad (3)$$

where  $V_i$  is the molar volume of component  $i$  in the mixture given by

$$V_i = \frac{M_i}{\rho_i} \quad (4)$$

where  $M_i$  and  $\rho_i$  are the molecular weight and density of the pure component.

Speed of sound ( $u$ ) along with the density ( $\rho$ ) data were employed to compute the isentropic compressibility ( $K_s$ ) and deviation in isentropic compressibility ( $\Delta K_s$ ) of binary and ternary liquid solutions. The isentropic compressibility for pure components and their mixtures has been calculated using the relation<sup>13</sup>

$$K_s = (u^2 \rho)^{-1} \quad (5)$$

The deviation in isentropic compressibility has been calculated using the relation

$$\Delta K_s = K_{s,m} - \sum_i^n x_i K_{s,i} \quad (6)$$

In this equation  $K_{s,m}$  and  $K_{s,i}$  are the isentropic compressibilities of mixture and pure component respectively.

$K_s^E$  of all the solutions under the present investigation is obtained from the procedure adopted by Benson et al<sup>24-25</sup> and others<sup>15, 16, 26</sup> using the following equations:

$$K_s^E = K_{s,m} - K_{s,id} \quad (7)$$

where

$$K_{s,m} = (u_m^2 \rho_m)^{-1} \quad (8)$$

and

$$K_{s,id} = \left[ \sum_i x_i \left\{ K_{s,i} + TV_i \alpha_i^2 / Cp_i \right\} - T \left( \sum_i x_i V_i \right) \left( \sum_i \phi_i \alpha_i \right)^2 / \sum_i x_i Cp_i \right] \quad (9) \quad ?$$

$K_T$

Here,  $\alpha_i$ ,  $Cp_i$ ,  $K_T$  and  $\phi_i$  are the thermal expansion coefficient, heat capacity at constant pressure, isothermal compressibility and volume fraction of  $i^{\text{th}}$  component.  $K_{s,i}$  is the isentropic compressibility of component  $i$ .

The experimental values of coefficient of thermal expansion ( $\alpha$ ) and isothermal compressibility ( $K_T$ ) of pure components are obtained from recently proposed relations.<sup>17</sup>

$$\alpha_i = \frac{75.6 \times 10^{-3}}{T^{1/9} \rho_i^{1/3} u_i^{1/2}} \quad (10)$$

$$K_{T,i} = \frac{1.71 \times 10^{-3}}{T^{4/9} \rho_i^{4/3} u_i^2} \quad (11)$$

where all the symbols have their usual meanings. In this equation  $u$ ,  $\rho$  and  $T$  are expressed in  $\text{ms}^{-1}$ ,  $\text{g cm}^{-3}$  and Kelvin.

Heat capacity at constant pressure ( $C_{p,i}$ ) and volume fraction ( $\phi_i$ ) of component liquids are calculated using following expressions

$$K_{T,i} - K_{s,i} = \frac{\alpha_i^2 T V_i}{C_{p,i}} \quad (12)$$

where  $T$  and  $V_i$  are the temperature in Kelvin and molar volume respectively.  
and

$$\phi_i = \frac{x_i V_i}{\sum x_i V_i} \quad (13)$$

where  $V_i$  is the molar volume of  $i^{\text{th}}$  component.

The values of excess molar volume and excess isentropic compressibility of all the binary liquid mixtures have been fitted by least square method using Redlich-Kister type polynomial equation

$$Y^E = x(1-x) \sum_{i=0}^n A_i (1-2x)^i \quad (14)$$

where  $Y^E$  may be  $V^E$  or  $K_s^E$  or  $\Delta K_s$

The values of the coefficients  $A_i$  of the above equation were obtained by the least square fit. The standard deviations were calculated using equation,

$$\sigma(Y^E) = \left[ \sum Y_{obs}^E - Y_{cal}^E / (m - n) \right]^{1/2} \quad (15)$$

where  $m$  is the total number of experimental points and  $n$  is the number of coefficients considered ( $n=5$ ) in the present calculation.

## Results and discussion

The excess molar volume,  $V^E$ , calculated from the measured density using eq (1), the deviation in isentropic compressibility ( $\Delta K_s$ ) and the values of excess isentropic compressibility,  $K_s^E$  calculated respectively from eqs (6) and (7) for two binary liquid mixtures viz. ethanol+hexane and ethanol+dodecane at 308.15 K are reported in tables 1 and 2 respectively. The values of both  $V^E$  and  $K_s^E$  were fitted to Redlich-Kister equation and shown graphically as a function of mole fraction of ethanol in figs 1, 2, 3 and 4. The results of isentropic compressibility and excess molar volume for ternary system namely ethanol+hexane+decane are recorded in table 3.

The coefficients ( $A_i$ ) evaluated by the least square method vide eqs (14) and (15) for  $V^E$  and  $K_s^E$  of the binary liquid mixtures are tabulated in table 4 along with the standard deviations.

The data of  $V^E$  and  $K_s^E$  for mixtures ethanol+hexane and ethanol+dodecane included in tables 1 and 2, and in figs 1, 2, 3 and 4 show that in all systems the different excess functions  $V^E$  and  $K_s^E$  are non-zero which indicate the presence of interactions between the components of the systems. The values of  $V^E$  and  $K_s^E$  for all the binary systems are positive over the entire composition range, but in the case of ethanol+hexane, the  $V^E$  values are negative at two mole fractions ( $x_1=0.7996$  and  $0.9469$ ).

As stated earlier, the positive values of excess molar volume  $V^E$  and excess isentropic compressibility  $K_s^E$  indicate the presence of weak interactions. Thus, perusal of sign and magnitude of excess functions  $V^E$  and  $K_s^E$  show that in both the binary liquid mixtures, the molecular interactions between the components of the mixtures are weak. In the present investigation, the positive values of  $V^E$  and  $K_s^E$  for both systems (ethanol+hexane and ethanol+dodecane) over entire composition range

of ethanol can be considered as arising from two types of interactions between the component molecules of the liquid mixtures. First is the interaction consisting mainly of dispersion forces or weak dipole-dipole interaction and making a positive contribution towards  $V^E$  and  $K_s^E$ . Second is the chemical specific interaction which include charge transfer forces, hydrogen bonds formation and other complex forming interactions, resulting in negative values of  $V^E$  and  $K_s^E$ . It is well known that alcohols are strongly self-associated through hydrogen bonding (protic) in pure state. The mixing of alkanes with ethanol tends to break the associates present in the alkanols molecules, resulting an increase in  $V^E$  and  $K_s^E$ . Thus, positive values of  $V^E$  and  $K_s^E$  suggest that molecules in solutions are loosely packed and easily compressible with increasing pressure and interactions are weak between components molecules in liquid mixtures.

Table 3 shows that in ternary system, ethanol+hexane+decane,  $V^E$  values are positive over the entire range of composition except two mole fractions ( $x_1=0.7175$  and  $0.9441$ ), suggesting weak interactions between the molecules in the system.

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Table - 1

Excess molar volume ( $V^E$ ), deviation in isentropic compressibility ( $\Delta K_s$ ) and excess isentropic compressibility ( $K_s^E$ ) of binary solution ethanol ( $x_1$ )+hexane ( $x_2$ ) at 308.15 K

$x_1$	$\rho$ (kg m <sup>-3</sup> )	$u$ (m s <sup>-1</sup> )	$V_m$ (10 <sup>-6</sup> m <sup>3</sup> mol <sup>-1</sup> )	$V^E$ (10 <sup>-6</sup> m <sup>3</sup> mol <sup>-1</sup> )	$K_{s,m}$ (TPa <sup>-1</sup> )	$\Delta K_s$ (TPa <sup>-1</sup> ) Eq(6)	$K_s^E$ (TPa <sup>-1</sup> ) Eq(7)
0.0486	655.2	1006.79	128.56	0.1353	150.57	9.5527	10.1008
0.1529	661.5	1009.24	121.01	0.1694	148.42	11.5857	13.1836
0.3513	675.9	1021.42	106.66	0.2456	141.81	12.9557	16.0054
0.5001	690.0	1032.16	95.83	0.2297	136.04	13.1551	16.7271
0.6472	708.5	1044.61	85.00	0.0941	129.35	12.3740	15.8689
0.7996	734.1	1065.05	73.71	-0.1126	120.09	9.2490	11.8952
0.9469	766.3	1102.10	62.90	-0.2137	107.44	2.5122	3.4092

**Table - 2**

**Excess molar volume ( $V^E$ ), deviation in isentropic compressibility ( $\Delta K_s$ ) and excess isentropic compressibility ( $K_s^E$ ) of binary solution ethanol ( $x_1$ ) + dodecane ( $x_2$ ) at 308.15 K**

$x_1$	$\rho$ ( $\text{kg m}^{-3}$ )	$u$ ( $\text{m s}^{-1}$ )	$V_m$ ( $10^{-6} \text{ m}^3 \text{ mol}^{-1}$ )	$V^E$ ( $10^{-6} \text{ m}^3 \text{ mol}^{-1}$ )	$K_{s,m}$ ( $\text{TPa}^{-1}$ )	$\Delta K_s(\text{TPa}^{-1})$ Eq(6)	$K_s^E(\text{TPa}^{-1})$ Eq(7)
0.2989	740.4	1185.83	179.90	0.1653	96.05	2.8595	2.0604
0.4002	741.9	1167.59	162.56	0.2329	98.87	4.2906	3.2753
0.5001	743.7	1156.25	145.48	0.3255	100.58	4.6342	3.4494
0.5488	744.8	1152.39	137.14	0.3534	101.11	4.4923	3.2454
0.6001	746.2	1148.08	128.34	0.3628	101.67	4.3543	3.0608
0.6996	750.1	1143.37	111.19	0.3126	101.98	3.3009	1.9890
0.8001	756.0	1137.41	93.80	0.1983	102.25	2.1938	1.0056
0.9002	764.5	1130.04	76.48	0.0794	102.43	1.0022	0.1789
0.9502	770.1	1124.85	67.86	0.0496	102.63	0.5171	0.0262

**Table - 3**

**Excess molar volume ( $V^E$ ) and isentropic compressibility  
( $K_{s,m}$ ) of ternary solution ethanol( $x_1$ )+hexane( $x_2$ )+decane( $x_3$ )  
at 308.15 K**

$x_1$	$x_2$	$\rho$ (kg m <sup>-3</sup> )	$u$ (m s <sup>-1</sup> )	$V_m$ (10 <sup>-6</sup> m <sup>3</sup> mol <sup>-1</sup> )	$V^E$ (10 <sup>-6</sup> m <sup>3</sup> mol <sup>-1</sup> )	$K_{s,m}$ (TPa <sup>-1</sup> )
0.0492	0.2480	706.8	1158.67	174.92	0.2831	105.39
0.1826	0.2132	711.2	1155.14	158.54	0.0882	105.38
0.3298	0.1748	714.5	1141.14	141.00	0.4128	107.48
0.4715	0.1378	719.8	1128.80	123.90	0.5119	109.03
0.6265	0.0974	730.4	1124.00	104.79	0.2113	108.37
0.7175	0.0737	741.8	1101.50	93.17	-0.3638	111.11
0.9441	0.0146	768.1	1097.71	65.91	-0.1217	108.05

Table - 4

Parameters of equation ( 14 ) and standard deviations

Ethanol+hexane						
	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma(Y^E)$
$V^E(10^{-6} \cdot m^3 \text{ mol}^{-1})$	0.9206	2.0695	2.3418	2.4576	-5.3900	0.0004
$Eq(6)-\Delta K_s \text{ (TPa}^{-1})$	52.4400	-11.1100	48.5000	120.3300	54.6500	0.0005
$Eq(7)-K_s^E \text{ (TPa}^{-1})$	66.7400	-14.4200	49.0100	120.2200	54.8600	0.0004
Ethanol+dodecane						
	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma(Y^E)$
$V^E(10^{-6} \cdot m^3 \text{ mol}^{-1})$	1.3034	-1.5253	-1.6906	4.1371	4.1742	0.0034
$Eq(6)-\Delta K_s \text{ (TPa}^{-1})$	18.5750	0.1120	-23.5480	-17.5910	-1.9430	0.0062
$Eq(7)-K_s^E \text{ (TPa}^{-1})$	13.8330	2.9950	-25.0420	-16.7200	-3.7580	0.0062

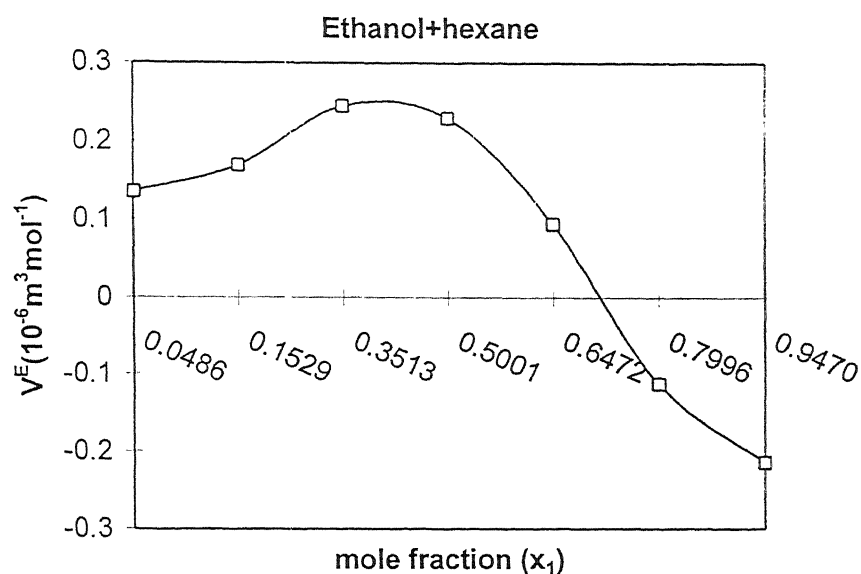


Fig 1. Excess volume,  $V^E$  of ethanol+hexane solution at 308.15K

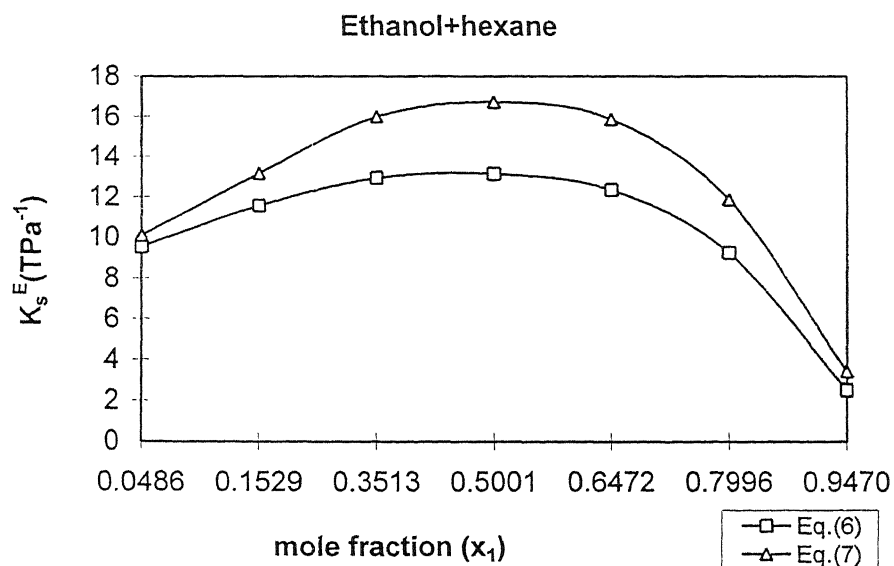


Fig 2. Excess isentropic compressibility,  $K_s^E$  of ethanol+hexane solution from eqs. (6) and (7) at 308.15K

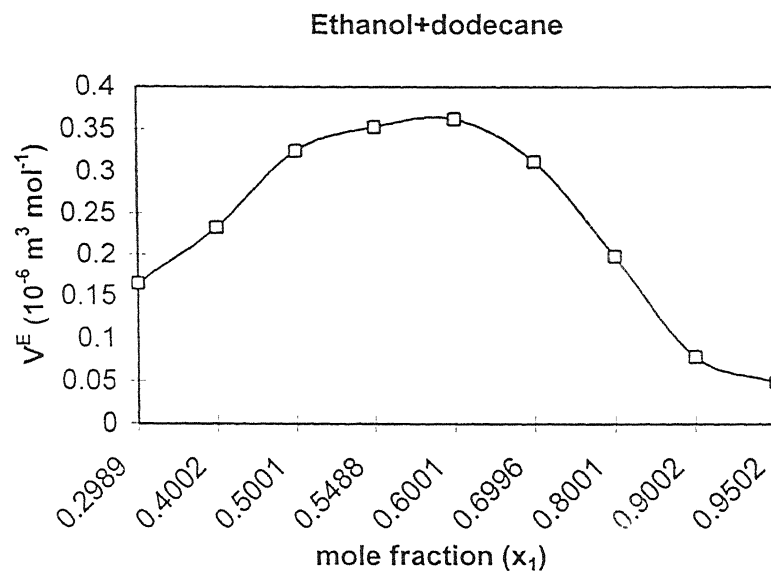


Fig 3. Excess volume,  $V^E$  of ethanol+dodecane solution at 308.15K

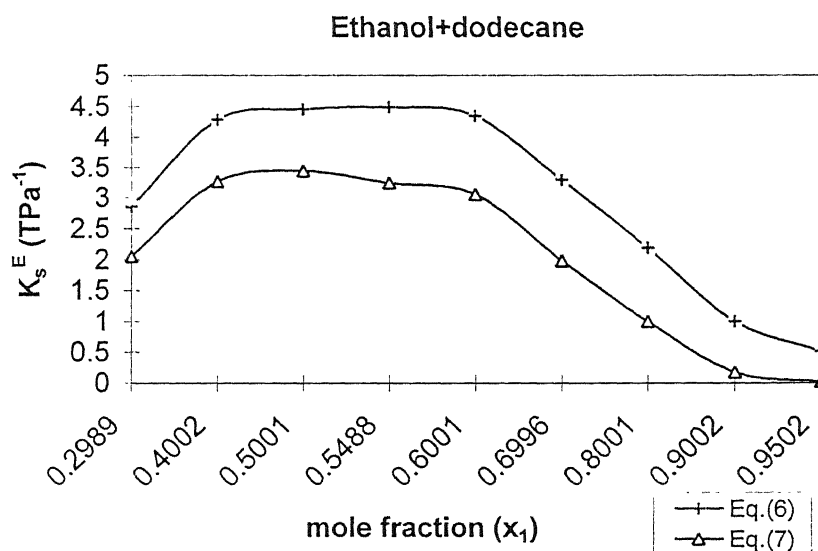


Fig 4. Excess isentropic compressibility,  $K_s^E$  of ethanol+dodecane solution from eqs. (6) and (7) at 308.15K

# **CHAPTER V**

## **Refractivity studies of binary and ternary solutions**

## Introduction

The knowledge of refractive index ( $n$ ) and molar refraction ( $R_m$ ) is useful for predicting many physico-chemical properties of liquid mixtures. Refractive index is used to evaluate the molar refraction and molecular connectivity which are used in predicting the structure of the liquid and their solutions. There are several empirical and semi empirical mixing rules for evaluating the refractive index of binary liquid solutions. The validity of various mixing rules as proposed by Lorentz-Lorenz (L-L), Gladstone-Dale (G-D), Weiner (W), Heller (H), Arago-Biot (A-B), Eykman (Eyk) and Oster (Os) relation has been tested by various workers during recent years<sup>1-4</sup>.

It was found that the L-L, G-D, Eyk and Os relations have performed well with less deviation from experimental values whereas W, H and A-B are found to be unsatisfactory, but deviations are not out of the experimental precision. Recently Pandey et al<sup>5,15-16</sup> and other workers<sup>6-7</sup> have also studied the relative validity of refractive index mixing rules for multicomponent liquid systems. Refractive index measurements in binary and multicomponent liquid mixtures have been made by several workers<sup>3,8-13</sup>. The values of refractive index of multicomponent systems have also been evaluated theoretically from the respective data of their binaries constituents<sup>17</sup>.

In the present work refractive indices ( $n$ ) of two binary liquid solutions viz. ethanol+hexane and ethanol+dodecane, and one ternary solution ethanol+hexane+decane are measured along with all the pure components at 308.15K. Using experimental values of refractive index, change in refractive indices  $\Delta n$ , and change in molar refraction  $\Delta R_m$  values have been calculated for all the systems and the results are fitted to Redlich-Kister polynomial equation. The refractive indices of all binary and ternary solutions have been evaluated theoretically using various mixing rules (L-L, G-D, W, H, A-B, Eyk and Os) from the experimental values of pure components of the mixtures. A comparative study of the validity, merits and demerits of all the mixing rules have also been made.



## Theoretical

The most important basis of various mixing rules,<sup>13</sup> which are used to calculate refractive index of binary and ternary liquid mixtures is the electromagnetic theory of light in which molecules are considered as dipoles or assemblies of dipole induced by an external field. The mixing rules which are used to calculate the refractive index of binary and ternary liquid solutions are as follows:

**Lorentz-Lorenz (L-L) relation:** L-L relation has widest applicability in predicting the refractive index of mixture from the refractive index and density of pure components. For ternary mixture it can be represented in weight fraction form as,

$$\left[ \frac{n_m^2 - 1}{n_m^2 + 2} \right] \frac{1}{\rho_m} = \left[ \frac{n_1^2 - 1}{n_1^2 + 2} \right] \frac{W_1}{\rho_1} + \left[ \frac{n_2^2 - 1}{n_2^2 + 2} \right] \frac{W_2}{\rho_2} + \left[ \frac{n_3^2 - 1}{n_3^2 + 2} \right] \frac{W_3}{\rho_3} \quad (1)$$

In terms of volume fraction form it can be written as,

$$\left[ \frac{n_m^2 - 1}{n_m^2 + 2} \right] = \left[ \frac{n_1^2 - 1}{n_1^2 + 2} \right] \phi_1 + \left[ \frac{n_2^2 - 1}{n_2^2 + 2} \right] \phi_2 + \left[ \frac{n_3^2 - 1}{n_3^2 + 2} \right] \phi_3 \quad (2)$$

where  $n_m$ ,  $n_1$ ,  $n_2$  and  $n_3$  are the refractive index of the liquid mixture and its pure components 1, 2 and 3 in the mixture respectively.  $\rho_m$ ,  $\rho_1$ ,  $\rho_2$  and  $\rho_3$  are their respective densities.  $W_1$ ,  $W_2$ ,  $W_3$  and  $\phi_1$ ,  $\phi_2$ ,  $\phi_3$  are the weight fractions and volume fractions of the pure components in liquid mixtures, which can be calculated from the relation

$$W_i = \frac{\phi_i \rho_i}{\rho_m} = \frac{x_i M_i}{M_{mix}} = \frac{x_i M_i}{\sum x_i M_i} \quad (3)$$

This is the relation between weight fraction, volume fraction and mole fraction.

The volume fraction is obtained as

$$\phi_i = \frac{c_i}{\rho_i} \quad (4)$$

$c_i$  is the concentration (g/ml) and  $\rho_i$  the density of  $i^{\text{th}}$  component.

### Gladstone-Dale [G-D] relation:

It can be expressed as,

$$(n_m - 1) = \phi_1(n_1 - 1) + \phi_2(n_2 - 1) + \dots \quad (5)$$

In an alternative form G-D relation may be given as,

$$\frac{n_m}{\rho_m} = \left[ \frac{(n_1 - 1)}{\rho_1} \right] W_1 + \left[ \frac{(n_2 - 1)}{\rho_2} \right] W_2 + \left[ \frac{(n_3 - 1)}{\rho_3} \right] W_3 \quad (6)$$

### Wiener relation (W) :

Like other relations, assuming volume additivity, this relation can be obtained by putting  $(1 - \phi_1)$  in place of  $\phi_1$  in the second form of L-L relation,

$$\left[ \frac{(n_m^2 - 1)}{(n_m^2 + 2)} - \frac{(n_1^2 - 1)}{(n_1^2 + 2)} \right] = \left[ \frac{(n_2^2 - 1)}{(n_2^2 + 2)} - \frac{(n_1^2 - 1)}{(n_1^2 + 2)} \right] \phi_2 + \left[ \frac{(n_3^2 - 1)}{(n_3^2 + 2)} - \frac{(n_1^2 - 1)}{(n_1^2 + 2)} \right] \phi_3 \quad (7)$$

on solving eq (7) the final obtained equation is

$$\left[ \frac{(n_m^2 - n_1^2)}{(n_m^2 + 2n_1^2)} \right] = \left[ \frac{(n_2^2 - n_1^2)}{(n_2^2 + 2n_1^2)} \right] \phi_2 + \left[ \frac{(n_3^2 - n_1^2)}{(n_3^2 + 2n_1^2)} \right] \phi_3 \quad (8)$$

It is clear from the above discussion that both Wiener and L-L relations give the same results if solution is ideal.

### Heller's (H) relation:

Heller relation can be obtained by substituting  $n_2/n_1=m_1$ , and  $n_3/n_2=m_2$ , assuming  $n_m \approx n_1$  in the above mentioned Wiener relation (8)

$$\left[ \frac{(n_m - n_1)(n_m + n_1)}{(n_m^2 + 2n_1^2)} \right] = \left[ \frac{(n_2^2 / n_1^2 - 1)}{(n_2^2 / n_1^2 + 2)} \right] \phi_2 + \left[ \frac{(n_3^2 / n_1^2 - 1)}{(n_3^2 / n_1^2 + 2)} \right] \phi_3$$

on rearranging the above equation, we get Heller's relation

$$\frac{n_m - n_1}{n_1} = \frac{3}{2} \left[ \left\{ \phi_2 \left( \frac{m_1^2 - 1}{m_1^2 + 2} \right) \right\} + \left\{ \phi_3 \left( \frac{m_2^2 - 1}{m_2^2 + 2} \right) \right\} \right] \quad (9)$$

The basis of the above equation is the Debye equation of light scattering.

Wiener and Heller both relations are valid only in the case of volume additivity i.e.  $\phi_i$

$$\phi_i = \frac{V_i}{\sum V_i}$$

### Arago-Biot (A-B) relation:

Arago-Biot proposed independently a relation for the evaluation of refractive index of binary and multicomponent liquid mixtures assuming volume additivity, which is given below

$$n_m = \phi_1 n_1 + \phi_2 n_2 + \dots \quad (10)$$

### Eykman's (Eyk) relation:

It can be expressed as

$$\left[ \frac{n_m^2 - 1}{n_m + 0.4} \right] = \left[ \frac{n_1^2 - 1}{n_1 + 0.4} \right] \frac{V_1}{V_m} + \left[ \frac{n_2^2 - 1}{n_2 + 0.4} \right] \frac{V_2}{V_m} + \left[ \frac{n_3^2 - 1}{n_3 + 0.4} \right] \frac{V_3}{V_m} \quad (11)$$

where  $V_1/V_m = \phi_1$  and  $V_2/V_m = \phi_2$ , and all symbols used here have their usual meaning.

### Oster (Os) relation:

Refractive index of mixture can be computed using Os relation as

$$\left[ \frac{(n_m^2 - 1)(2n_m^2 + 1)}{n_m^2} \right] = \left[ \frac{(n_1^2 - 1)(2n_1^2 + 1)}{n_1^2} \right] \phi_1 + \left[ \frac{(n_2^2 - 1)(2n_2^2 + 1)}{n_2^2} \right] \phi_2 \quad (12)$$

The molar refraction ( $R_m$ ) can be calculated from refractive index values using the relation<sup>16</sup>

$$R_m = \frac{n^2 - 1}{n^2 + 2} V_m \quad (13)$$

where  $V_m$  is the molar volume of mixture and calculated from the relation

$$V_m = \frac{\sum x_i M_i}{\rho_m}$$

where  $x_i$  and  $M_i$  are the mole fraction and molecular weight of  $i^{\text{th}}$  component in the mixture respectively.

The deviation in molar refraction,  $\Delta R_m$  can be evaluated from the expression

$$\Delta R_m = R_m - \sum R_{m,i} x_i \quad (14)$$

where  $R_{m,i}$  is the molar refraction of pure component i.

The deviation in refractive index has been calculated using equation

$$\Delta n = n_m - n_{id} \quad (15)$$

where  $n_m$  is the refractive index of mixture and  $n_{id}$  is the ideal refractive index, which can be obtained as,

$$n_{id} = \sum x_i n_i \quad (16)$$

The values of  $\Delta n$  and  $\Delta R_m$  of all binary mixtures have been fitted by least square method using Redlich-Kister type polynomial equation

$$Y^E = x(1-x) \sum_{i=0}^n A_i (1-2x)^i \quad (17)$$

where  $Y^E$  may be  $\Delta n$  or  $\Delta R_m$ .

The values of the coefficients  $A_i$  of the above equation were obtained by the least square fit. The standard deviations were calculated using equation,

$$\sigma(Y^E) = \left[ \sum Y_{obs}^E - Y_{cal}^E / (m-n) \right]^{1/2} \quad (18)$$

where m is the total number of experimental points and n is the number of coefficients considered (n=5) in the present calculation.

## Results and discussion

The experimental values of refractive index ( $n$ ), change in refractive index ( $\Delta n$ ) and change in molar refraction ( $\Delta R_m$ ) upon mixing were calculated using experimental data of refractive indices of two binary solutions viz. ethanol+hexane and ethanol+dodecane and one ternary solution namely ethanol+hexane+decane at 308.15K. The results are summarized in tables 1, 2 and 3 respectively. The refractive index has also been computed theoretically using various mixing rules viz. L-L, G-D, W, H, A-B, Eyk and Os for the same solutions at 308.15K and reported in table 1. The results of computation of refractive index using various mixing rules have been discussed in terms of average percentage deviations (APD).

The values of change in refractive index ( $\Delta n$ ) and change in molar refraction ( $\Delta R_m$ ) upon mixing were fitted to Redlich-Kister polynomial type equation. The coefficients  $A_i$  and standard deviations were estimated by least square method and listed in table 4.

A careful study of table 1 shows that for the system ethanol+hexane, the values of change in refractive index and change in molar refraction are negative over the entire composition range, except two mole fractions ( $x_1 = 0.1259$  and  $0.3513$ ), the values of  $\Delta n$  are positive.

As table 2 shows that for the system ethanol+dodecane, both positive and negative values of  $\Delta n$  and  $\Delta R_m$  were obtained. It is also observed that the magnitudes of  $\Delta n$  and  $\Delta R_m$  are greater in system ethanol+dodecane than those of system ethanol+hexane. It may be due to the increase in size of alkane molecules.

For ternary system (table 3) viz. ethanol+hexane+decane, the values of  $\Delta n$  and  $\Delta R_m$  are positive over the entire range of concentration. But  $\Delta R_m$  values are negative at two mole fractions ( $x_1 = 0.7173$  and  $0.9441$ ).

The deviation in molar refraction,  $\Delta R_m$ , gives more information than the change in refractive index ( $\Delta n$ ), about the mixture process because it takes into account the electronic perturbation of molecular orbital during liquid mixture process,<sup>4</sup> and molar refraction is also directly related to the dispersion forces. The positive values of  $\Delta R_m$  for mixtures indicate towards the higher dispersion forces in the mixtures than in pure liquids, whereas negative  $\Delta R_m$  values of mixtures indicate that the dispersion forces are lower in the mixtures than in pure liquids.<sup>10</sup>

The results of refractive index calculated theoretically using various mixing rules for two binary and one ternary mixtures have been analysed in terms of average percentage deviations (APD) ~~deviations~~ which are tabulated in tables 1, 2 and 3. A comparison of experimental results of refractive index, and the results obtained from various mixing rules indicate that there is a good agreement between the experimental and theoretical values. For the system ethanol+hexane the order of APD is  $H < G-D < Eky < L-L < Os < W < A-B$ , whereas for system ethanol+dodecane the order is as follows  $H < G-D < Eky < Os < L-L < W < A-B$ . The order of APD shows that H, G-D and Eky mixing rules provide excellent agreement with the experimental values than the other relations, but the deviations resulted from other relations are not out of the experimental precision. It is also observed that the magnitude of APD for system ethanol+dodecane is higher than the system ethanol+hexane like the magnitude of  $\Delta n$  and  $\Delta R_m$ .

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Table - 1

Values of refractive indices, change in refractive indices ( $\Delta n$ ) and change in molar refraction ( $\Delta R_m$ ) upon mixing for ethanol+hexane solution at 308.15K

$x_1$	$n_{\text{exp}}$	$R_{m,\text{exp}}$	$\Delta n$	$\Delta R_m$	L-L	G-D	W	H	A-B	Eyk	Os
0.0486	1.3710	29.3624	-0.0003	-0.0039	1.3717	1.3738	1.3717	1.3716	1.3717	1.3711	1.3711
0.1529	1.3700	27.5115	0.0003	-0.0583	1.3709	1.3728	1.3709	1.3709	1.3709	1.3709	1.3709
0.3513	1.3670	24.0312	0.0003	-0.1213	1.3691	1.3703	1.3691	1.3691	1.3691	1.3691	1.3691
0.5001	1.3640	21.4127	-0.0005	-0.1769	1.3674	1.3683	1.3674	1.3674	1.3674	1.3674	1.3674
0.6472	1.3620	18.9046	-0.0003	-0.1513	1.3652	1.3663	1.3652	1.3652	1.3653	1.3652	1.3653
0.7996	1.3590	16.2933	-0.0010	-0.1377	1.3624	1.3639	1.3624	1.3624	1.3624	1.3624	1.3624
0.9469	1.3570	13.8342	-0.0008	-0.0580	1.3587	1.3602	1.3587	1.3587	1.3587	1.3587	1.3587
APD					-0.1598	-0.0027	-0.1603	-0.0016	-0.1607	-0.1544	-0.1557

Table - 2

Values of refractive indices, change in refractive indices ( $\Delta n$ ) and change in molar refraction ( $\Delta R_m$ ) upon mixing for ethanol+dodecane solution at 308.15K

$x_1$	$n_{exp}$	$R_{m,exp}$	$\Delta n$	$\Delta R_m$	L-L	G-D	W	H	A-B	Eyk	Os
0.2989	1.4145	44.9602	0.0154	0.3364	1.4110	1.4107	1.4110	1.4107	1.4111	1.4111	1.4111
0.4002	1.4083	40.0709	0.0153	0.0193	1.4081	1.4076	1.4082	1.4078	1.4082	1.4082	1.4083
0.5001	1.3945	34.7612	0.0075	-0.7814	1.4045	1.4039	1.4047	1.4044	1.4048	1.4047	1.4049
0.5488	1.3855	32.0930	0.0014	-1.2514	1.4025	1.4017	1.4026	1.4024	1.4027	1.4027	1.4029
0.6001	1.3750	29.4801	-0.0060	-1.5489	1.4001	1.3992	1.4002	1.4000	1.4003	1.3976	1.3981
0.6996	1.3551	24.3195	-0.0199	-2.2185	1.3943	1.3935	1.3945	1.3943	1.3946	1.3919	1.3924
0.8001	1.3429	19.8785	-0.0261	-2.1234	1.3863	1.3858	1.3865	1.3864	1.3866	1.3843	1.3848
0.9002	1.3508	16.5330	-0.0122	-0.9508	1.3749	1.3747	1.3750	1.3750	1.3751	1.3736	1.3740
0.9502	1.3670	15.2586	0.0070	0.0316	1.3670	1.3669	1.3671	1.3671	1.3672	1.3663	1.3665
<hr/>											
APD											
-1.1286 -0.0109 -1.1378 -0.0112 -1.1436 -1.0577 -1.0789											

Table - 3

Values of refractive indices, change in refractive index ( $\Delta n$ ) and change in molar refraction ( $\Delta R_m$ ) upon mixing for the system ethanol+hexane+decane at 308.15K

$x_1$	$x_2$	$n_{exp}$	$R_{mexp}$	$\Delta n$	$\Delta R_m$	L-L	G-D	W	H	A-B	Eyk	Os
0.0492	0.2480	1.4020	42.5922	0.0061	0.2157	1.4069	1.3998	1.3998	1.3873	1.3998	1.3934	1.3941
0.1826	0.2132	1.4000	38.4332	0.0096	0.1812	1.3905	1.3962	1.3962	1.3849	1.3962	1.4032	1.4026
0.3298	0.1748	1.3980	34.0304	0.0136	0.3294	1.3809	1.3922	1.3921	1.3821	1.3922	1.4045	1.4035
0.4715	0.1378	1.3950	29.7050	0.0164	0.3844	1.3694	1.3873	1.3872	1.3788	1.3873	1.4069	1.4052
0.6265	0.0974	1.3850	24.5578	0.0127	0.0301	1.3533	1.3804	1.3804	1.3740	1.3804	1.4121	1.4093
0.7175	0.0737	1.3770	21.4299	0.0085	-0.2835	1.3415	1.3753	1.3753	1.3705	1.3753	1.4180	1.4141
0.9441	0.0146	1.3640	14.6922	0.0047	-0.0150	1.3001	1.3575	1.3575	1.3581	1.3575	1.4302	1.4231
<b>APD</b>												
						2.3506	0.7896	0.7902	1.1346	0.7896	-1.5699	-1.3722

Table - 4

Parameters of equation ( 17 ) and standard deviations

Ethanol+hexane						
	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma(Y^E)$
$\Delta n$	0.0025	0.0098	-0.0074	-0.0046	-0.0106	0.0001
$\Delta R_m$	-0.6438	0.0412	-0.1762	0.6709	0.219	0.009
Ethanol+dodecane						
	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma(Y^E)$
$\Delta n$	0.0318	0.2216	-0.3474	-0.1024	0.3481	0.0006
$\Delta R_m$	-0.3089	2.2949	-3.7473	-0.7115	7.5684	0.0048

# **CHAPTER VI**

## **Theoretical evaluation of viscosity of multicomponent solutions**

## Introduction

The knowledge of thermodynamic and transport properties of multicomponent liquid systems are essential in many industrial applications such as design calculation, heat transfer, mass transfer and fluid flow etc. Viscous flow properties of liquid or liquid mixtures are very sensitive to temperature and pressure.

It is impractical to measure viscosity at all external conditions of interest, therefore, method for estimation of viscosities of multicomponent mixtures are not only of theoretical but also of great practical interest. To explain the viscous flow mechanism various theories have been proposed. Some of them explain the phenomenon in terms of the transport properties while some are concerned with the statistical thermodynamics. Number of viscosity equations for the study of liquids and liquid mixtures are discussed in great detail by Reid et al<sup>1</sup> and Glastone et al<sup>2</sup>. The principle of corresponding state<sup>3</sup> has also been used to describe the viscosity of liquids and liquid mixtures. Many workers<sup>4,7</sup> used group contribution method to correlate liquid viscosities of molecular structure. In the course of time, a number of empirical and semi empirical equations have been used to calculate the viscosity of liquid mixtures using pure component data<sup>20-22</sup>. These empirical and semiempirical relations relate viscosity to the molar volume, ultrasonic velocity and free space. Thermodynamic and statistical study of viscosity provides the knowledge of molecular structure of liquid and liquid mixtures and also information in terms of parameters i.e. molecular size and shape, condensation effect, lattice distortion and disorder parameters, steric hinderence contribution and extent of non-linearity of liquid mixtures.

A lot of work has been done on the experimental measurement of viscosity and its theoretical interpretation in binary and ternary liquid mixtures<sup>7</sup>. Various liquid viscosity models viz. Frenkel, Kendall, Munroe, Additive, Bingham, Hind-Ubbelhode etc. proposed for binary liquid mixtures of non-electrolytes, have been recently<sup>8</sup> extended for predicting the viscosity of multicomponent liquid mixtures. Comparative study of these empirical models have been done in the case of ternary and quaternary liquid mixtures. Statistical theory of Flory et al<sup>9</sup> and Eyring<sup>10</sup> (Significant structure

theory) were also applied very recently<sup>11,12</sup> to evaluate theoretically the viscosity of multicomponent non-electrolyte solutions.

The Bertrand-Acree-Burchfield (BAB) approach has also been extended to multicomponent systems<sup>15,16</sup> in which the properties of multicomponent systems are estimated from the properties of its constituent binaries. Pandey et al<sup>17</sup> applied Sutherland Wassiljewa relation,<sup>18</sup> based on the theory of multicomponent gas mixtures to evaluate the viscosity of liquid mixtures.

In the present chapter an attempt has been made at the problem of viscosity of multicomponent liquid solutions. Here, Sutherland Wassiljewa relation has been applied to compute the viscosity of multicomponent liquid systems. In the present context this approach has been applied on a wide spectrum of binary, ternary and quaternary liquid solutions. The results are found to be quite encouraging as evidenced from the results of calculation. Moreover, for computing the viscosities of mixtures, only the experimental values of viscosity and molecular mass of pure components along with two adjustable parameters  $A_{ij}$  and  $A_{ji}$  are required. These parameters called Wassiljewa coefficients are well known coefficients in the molecular theory of gases and their physical significance has been very recently<sup>20</sup> discussed. The present approach has been applied to nine binary mixtures at two temperatures (308.15K and 318.15K), one ternary and one quaternary mixture. The experimental data of viscosity of liquid mixtures are taken from the literature<sup>16,21,22</sup>. The results are discussed in terms of the percentage deviations to test the validity of the equation. The equation has also been found very versatile since it is able to predict the maxima and minima in the viscosity versus composition curve, in case of binary liquid mixtures, which was not predicted by the earlier viscosity relations<sup>19</sup>.

## Theoretical

The Sutherland Wassiljewa equation expressed as

$$\eta_m = \frac{\sum_i x_i \eta_i}{\sum_j A_{ij} x_j} \quad (1)$$

where  $x_i$  is the mole fraction of the  $i^{\text{th}}$  component and  $A_{ij}$  is the Wassiljewa coefficient interpreted by Gery et al<sup>18</sup> and Pandey et al<sup>8</sup> as the ratio of the efficiencies with which molecules  $j$  and  $i$  impede the transport of momentum by molecules  $i$ . The above eq (1) was given independently by Sutherland (1895), Wassiljewa (1904) and Hirschfelder (1958), their approaches were essentially different. Sutherland's derivations were based on the kinetic theory whereas Wassiljewa derived it on the basis of the theory of mean free path. Hirschfelder's approximation was based on the Chapman<sup>14</sup> and Enskog's<sup>15</sup> kinetic theory. The theory of mean free path and Chapman-Enskog theory has been discussed by L. Monchick<sup>22</sup>.

For binary mixtures the above eq (1) can be written as

$$\eta_m = \frac{x_1 \eta_1}{A_{12} x_2 + x_1} + \frac{x_2 \eta_2}{A_{12} x_2 + x_1} \quad (2)$$

For ternary mixtures

$$\eta_m = \frac{x_1 \eta_1}{A_{12} x_2 + A_{13} x_3 + x_1} + \frac{x_2 \eta_2}{A_{21} x_1 + A_{23} x_3 + x_2} + \frac{x_3 \eta_3}{A_{31} x_1 + A_{32} x_2 + x_3} \quad (3)$$

For quaternary mixtures

$$\eta_m = \frac{x_1 \eta_1}{A_{12} x_2 + A_{13} x_3 + A_{14} x_4 + x_1} + \frac{x_2 \eta_2}{A_{21} x_1 + A_{23} x_3 + A_{24} x_4 + x_2} + \frac{x_3 \eta_3}{A_{31} x_1 + A_{32} x_2 + A_{34} x_4 + x_3} + \frac{x_4 \eta_4}{A_{41} x_1 + A_{42} x_2 + A_{43} x_3 + x_4} \quad (4)$$



The Wassiljewa coefficient  $A_{ij}$  is independent of composition. Thus, viscosity of multicomponent mixtures can be predicted successfully from values of  $A_{ij}$  deduced from the measurements of binary liquid mixtures. Secondly the temperature dependence of  $A_{ij}$  is smaller than the experimental error. The Wassiljewa-Sutherland eq (1) is non-linear, flexible and capable of explaining even maxima or minima in viscosity composition curve.

A new empirical form has been given to the Wassiljewa coefficient  $A_{ij}$  to give the best possible result in case of liquids.

The Wassiljewa coefficient  $A_{ij}$  can be expressed as

$$A_{ij} = \frac{1}{4} \left[ 1 + \left( \frac{\eta_i}{\eta_j} \right)' \left( \frac{M_j}{M_i} \right)' \right]^2 \quad (5)$$

Where  $\eta_i$  and  $\eta_j$  are respectively the viscosities of i and j components and  $M_i$  and  $M_j$  are the molecular weight of components i and j.

## Results and discussion

The viscosities of several binary mixtures of alkyl alkanoate (methyl or ethyl propanoate and butanoate) –hydrocarbon and halogen derivatives (n-heptane, benzene, chlorobenzene and 1,1,2,2-tetrachloroethane) have been calculated at 308.15K and 318.15K using Sutherland-Wassiljewa equation. In addition to these binary mixtures, this equation has also been applied to one ternary and one quaternary liquid mixture at 298.15 K.

The results obtained from computation are compared with experimental values and reported in tables 1, 2 and 3 respectively. The experimental data for the present study have been taken from the literature<sup>16, 21-22</sup>.

Systems under present investigation are

## **Binary Systems**

1. Methyl propanoate+heptane
2. Methyl propanoate+benzene
3. Methyl propanoate+chlorobenzene
4. Methyl propanoate+tetrachloroethane
5. Methyl butanoate+heptane
6. Methyl butanoate+chlorobenzene
7. Ethyl propanoate+benzene
8. Ethyl propanoate+chlorobenzene
9. Ethyl butanoate+benzene

## **Ternary system**

Toluene+heptane+hexane

## **Quaternary system**

Carbontetrachloride+cyclohexane+benzene+toluene

A careful study of tables 1 and 2 shows that for binary systems, the agreement between the experimental values and calculated values of viscosities are satisfactory. The percentage deviation values for all binary systems vary from 0.00% to 5.21%. It is evident from table 3 that for ternary and quaternary system, the percentage deviations are found to lie between 0.03% to 3.88%, which shows better agreement

between experimental and calculated values of viscosities. The percentage deviation values indicate the validity of the Sutherland-Wasiljewa equation. The values of viscosity ( $\eta_m$ ) are found to be highest for the system ethyl butanoate+tetrachloroethane at 308.15K followed by those of ethyl propanoate+tertachloethane and those of methylpropanoate+tetrachloroethane. The maximum percentage deviations are observed for system ethyl propanoate+heptane at 308.15K followed by methyl butanoate+chlorobenzene at the same temperature. Another interesting observation is that for most of the systems under consideration the percentage deviation are found to lower with the increase in temperature (318.15K).

Previously reported values<sup>21</sup> of ultrasonic velocity for all the mixtures containing benzene and chlorobenzene as one of the components fall smoothly in linear fashion with the exception of ethyl butanoate+benzene in which a rectilinear dependence is seen. Further the experimental values of ultrasonic velocity for the binary mixture containing either n-heptane or 1,1,2,2-tetrachloroethane also show a smooth increase. Furthermore,  $K_s^E$  values computed<sup>21</sup> for the binary system of n-heptane with all the four esters at both the temperature were found to be large positive over the entire mole fraction range. The temperature coefficient were found to be positive for two methyl and two ethyl esters-n-heptane mixture and decreased by almost half the magnitude when the alkyl chain length of R and RCOOR' was increased. On the other hand the  $K_s^E$  values at equimolar concentration for the methyl esters-benzene, -chlorobenzene were found to be negative with increase in molar volume of R from propanoate to butanoate. Also the  $K_s^E$  values for ethyl propanoate and ethyl butanoate with 1,1,2,2-tetrachloroethane were found to show very similar values at both the temperatures, but the temperature coefficient values for all these mixtures were found to be negative. These observation point towards large and negative permitivity deviations and excess molar polarizations indicating decreased degree of alingment in ester-dipoles as a result of weakening of dipolar forces in ester molecules in the presence of unlike n-heptane. It is also observed that with the repacement of n-heptane by benzene, chlorobenzene or 1,1,2,2-tetrachloethane the excess volumes decreased systematically with increases in relative permitivity and molar polarization. These changes can also be explained by considering the over

balance of  $n-\pi$  as well as O-Cl type specific interactions between the lone pair of electrons on carbonyl group ester and  $\pi$ -electrons aromatic ring and Cl-group of the hydrocarbons containing chlorine.

All these effects are seen to have an impact on the computed viscosity values for the binary systems under investigation.

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Table - 1

## Viscosity of alkyl alkanoate - hydrocarbon mixtures at 308.15 K

## MP+heptane

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0447	0.356	0.354	0.5789
0.1083	0.361	0.355	1.5285
0.1932	0.367	0.358	2.3530
0.3018	0.375	0.362	3.4052
0.4146	0.384	0.369	3.8064
0.5227	0.392	0.377	3.9421
0.5693	0.396	0.381	3.8903
0.7002	0.408	0.395	3.1744
0.7986	0.417	0.407	2.4120
0.9016	0.427	0.421	1.4122
0.9509	0.432	0.429	0.6874

## MP+benzene

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0415	0.532	0.530	0.3713
0.1037	0.525	0.520	0.8791
0.2041	0.513	0.505	1.5849
0.3026	0.502	0.492	2.0572
0.4053	0.492	0.480	2.3469
0.4569	0.486	0.474	2.5252
0.6013	0.472	0.462	2.1475
0.7026	0.463	0.453	2.0947
0.8018	0.454	0.447	1.4975
0.9039	0.445	0.441	0.8959
0.9674	0.440	0.438	0.3814

## MP+chlorobenzene

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0485	0.662	0.646	2.3831
0.0993	0.648	0.635	2.0249
0.2038	0.621	0.612	1.4021
0.2614	0.606	0.599	1.1473
0.4087	0.569	0.567	0.4137
0.4556	0.558	0.556	0.3638
0.6041	0.523	0.523	0.0311
0.7011	0.501	0.503	-0.3654
0.8064	0.478	0.479	-0.2178
0.9054	0.457	0.457	-0.0560
0.9486	0.448	0.448	-0.0748

## MP+tetrachloroethane

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0501	1.336	1.352	-1.2355
0.1021	1.266	1.296	-2.3874
0.2031	1.140	1.186	-4.0785
0.302	1.026	1.078	-5.0292
0.3398	0.986	1.037	-5.2140
0.5038	0.823	0.865	-5.1390
0.6012	0.736	0.769	-4.5481
0.6946	0.658	0.681	-3.5282
0.7988	0.577	0.591	-2.4089
0.9016	0.503	0.509	-1.1705
0.9481	0.471	0.474	-0.5678

**MB+heptane**

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0525	0.360	0.357	0.7069
0.156	0.373	0.366	1.8352
0.1959	0.378	0.369	2.4117
0.2969	0.392	0.379	3.2830
0.4989	0.421	0.406	3.5966
0.5971	0.436	0.421	3.5106
0.7995	0.470	0.459	2.2841
0.8524	0.479	0.470	1.8738
0.9236	0.492	0.487	0.9719
0.9531	0.497	0.494	0.6456
0.9825	0.503	0.501	0.3377

**MB+chlorobenzene**

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0851	0.731	0.648	11.2990
0.1025	0.725	0.647	10.8143
0.2257	0.690	0.630	8.7561
0.3019	0.670	0.621	7.2713
0.4004	0.644	0.607	5.7163
0.5036	0.618	0.593	4.0068
0.5911	0.596	0.580	2.7635
0.6834	0.575	0.564	1.8823
0.8223	0.544	0.541	0.4827
0.8997	0.527	0.525	0.3669
0.9522	0.516	0.515	0.1707

**EP+benzene**

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0521	0.532	0.530	0.4319
0.0984	0.528	0.525	0.6135
0.2018	0.520	0.513	1.2633
0.3029	0.512	0.503	1.6741
0.4009	0.504	0.495	1.8315
0.4991	0.497	0.487	2.0675
0.5982	0.491	0.481	1.9634
0.7114	0.483	0.475	1.7503
0.8042	0.478	0.472	1.2338
0.8989	0.472	0.469	0.7383
0.9200	0.471	0.468	0.7043

**EP+chlorobenzene**

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0485	0.663	0.647	2.4232
0.1030	0.650	0.636	2.1419
0.1976	0.628	0.616	1.8692
0.3070	0.603	0.594	1.4977
0.3981	0.583	0.576	1.2353
0.4981	0.562	0.557	0.9208
0.6116	0.539	0.535	0.7782
0.7034	0.521	0.519	0.4341
0.7992	0.503	0.501	0.4256
0.9000	0.485	0.484	0.1437
0.9478	0.476	0.476	0.0346

**EB+benzene**

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0473	0.539	0.534	0.9048
0.0990	0.541	0.531	1.8346
0.1937	0.545	0.528	3.0606
0.2987	0.549	0.526	4.1567
0.4059	0.553	0.527	4.7062
0.4998	0.557	0.529	4.9763
0.5753	0.560	0.533	4.7617
0.7021	0.565	0.541	4.1750
0.7978	0.568	0.550	3.2140
0.9030	0.572	0.562	1.7999
0.9514	0.574	0.569	0.8969

Table - 2

## Viscosity of alkyl alkanoate - hydrocarbon mixtures at 318.15K

## MP+heptane

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0447	0.323	0.322	0.4326
0.1083	0.328	0.326	0.7163
0.1932	0.335	0.332	0.9510
0.3018	0.344	0.34	1.2560
0.4146	0.354	0.349	1.4999
0.5227	0.364	0.359	1.4821
0.5693	0.369	0.363	1.6029
0.7002	0.382	0.377	1.3488
0.7986	0.393	0.389	0.9406
0.9016	0.404	0.402	0.5707
0.9509	0.410	0.409	0.2658

## MP+benzene

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0415	0.467	0.466	0.3017
0.1037	0.464	0.461	0.5591
0.2041	0.458	0.453	1.0023
0.3026	0.452	0.446	1.3005
0.4053	0.446	0.440	1.3688
0.4569	0.443	0.437	1.4157
0.6013	0.436	0.430	1.2825
0.7026	0.430	0.425	1.2521
0.8018	0.425	0.430	-1.0697
0.9039	0.421	0.418	0.5977
0.9674	0.418	0.417	0.1238

## MP+chlorobenzene

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0485	0.597	0.598	-0.2143
0.0993	0.586	0.589	-0.4988
0.2038	0.565	0.57	-0.9627
0.2614	0.553	0.59	-6.7054
0.4087	0.524	0.531	-1.3689
0.4556	0.515	0.522	-1.4058
0.6041	0.487	0.493	-1.3014
0.7011	0.469	0.475	-1.3232
0.8064	0.450	0.454	-0.9305
0.9054	0.432	0.434	-0.3814
0.9486	0.425	0.426	-0.2721

## MP+tetrachloroethane

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0501	1.218	1.214	0.3142
0.1021	1.157	1.149	0.6991
0.2031	1.046	1.032	1.3842
0.302	0.947	0.927	2.0795
0.3398	0.911	0.889	2.3682
0.5038	0.765	0.741	3.1863
0.6012	0.687	0.664	3.3651
0.6946	0.617	0.597	3.2373
0.7988	0.544	0.528	2.9109
0.9016	0.476	0.468	1.7747
0.9481	0.447	0.443	0.9874



**MB+heptane**

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0525	0.326	0.326	0.0874
0.1560	0.339	0.337	0.6160
0.1959	0.344	0.341	0.9230
0.2969	0.357	0.352	1.5258
0.4989	0.386	0.379	1.7756
0.5971	0.401	0.397	0.9044
0.7995	0.433	0.427	1.4543
0.8524	0.442	0.437	1.2160
0.9236	0.455	0.451	0.8739
0.9531	0.460	0.458	0.5056
0.9825	0.466	0.465	0.1589

**MB+chlorobenzene**

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0851	0.594	0.601	-1.1733
0.1025	0.591	0.600	-1.4526
0.2257	0.573	0.588	-2.5920
0.3019	0.562	0.580	-3.1850
0.4004	0.548	0.567	-3.4497
0.5036	0.534	0.552	-3.4208
0.5911	0.522	0.540	-3.4829
0.6834	0.509	0.527	-3.4354
0.8223	0.491	0.504	-2.5649
0.8997	0.482	0.489	-1.5495
0.9522	0.475	0.479	-0.8542

**EP+benzene**

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0521	0.468	0.470	-0.4830
0.0984	0.466	0.470	-0.9045
0.2018	0.462	0.469	-1.6034
0.3029	0.458	0.468	-2.2447
0.4009	0.454	0.465	-2.3851
0.4991	0.451	0.462	-2.4880
0.5982	0.448	0.459	-2.5596
0.7114	0.444	0.453	-2.0168
0.8042	0.441	0.448	-1.5123
0.8989	0.439	0.443	-0.9841
0.9200	0.438	0.441	-0.6593

**EP+chlorobenzene**

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0485	0.597	0.598	-0.1000
0.1030	0.587	0.588	-0.2046
0.1976	0.569	0.570	-0.2047
0.3070	0.549	0.550	-0.2311
0.3981	0.533	0.534	-0.2788
0.4981	0.515	0.517	-0.3420
0.6116	0.496	0.498	-0.3502
0.7034	0.481	0.483	-0.3353
0.7992	0.466	0.467	-0.1520
0.9000	0.451	0.451	-0.0302
0.9478	0.444	0.444	-0.0665

**EB+benzene**

x	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0473	0.473	0.470	0.7170
0.0990	0.477	0.471	1.2750
0.1937	0.484	0.472	2.4357
0.2987	0.491	0.476	3.0803
0.4059	0.499	0.481	3.5176
0.4998	0.505	0.486	3.7532
0.5753	0.510	0.491	3.7369
0.7021	0.519	0.502	3.1903
0.7978	0.525	0.512	2.4511
0.9030	0.532	0.525	1.2668
0.9514	0.535	0.531	0.7236

Table - 3

## Viscosity of ternary and quaternary liquid mixtures at 298.15 K

## Toluene+heptane+hexane

$x_1$	$x_2$	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.1210	0.1838	0.337	0.335	0.3354
0.1459	0.2011	0.344	0.341	1.0130
0.1698	0.2170	0.351	0.346	1.5448
0.1929	0.2358	0.359	0.353	1.6461
0.2160	0.2544	0.366	0.359	2.0258
0.2390	0.2726	0.374	0.366	2.2545
0.2641	0.2875	0.382	0.372	2.5706
0.2849	0.3060	0.390	0.379	2.8262
0.3088	0.3222	0.398	0.384	3.3828
0.3330	0.3391	0.406	0.393	3.4079
0.3559	0.3553	0.415	0.400	3.6613
0.3760	0.3735	0.423	0.406	3.8804
0.3983	0.3908	0.431	0.415	3.8808
0.4204	0.3974	0.439	0.423	3.5433
0.4433	0.4045	0.447	0.442	1.1907

## Carbon tetrachloride+Cyclohexane+Benzene+Toluene

$x_1$	$x_2$	$x_3$	$\eta_{cal}$ (mPas)	$\eta_{exp}$ (mPas)	$\Delta\%$
0.0482	0.2843	0.3422	0.687	0.670	2.5573
0.0890	0.2812	0.3422	0.700	0.688	1.7312
0.1287	0.2614	0.3517	0.707	0.697	1.3844
0.2055	0.2223	0.4020	0.722	0.722	0.0046
0.2417	0.2258	0.3875	0.734	0.726	1.0272
0.2823	0.1804	0.4335	0.735	0.739	-0.5131
0.3061	0.0369	0.3963	0.705	0.696	1.2307
0.3109	0.0749	0.3530	0.716	0.720	-0.5908
0.3206	0.1614	0.4469	0.742	0.764	-2.9988
0.1961	0.3151	0.0948	0.741	0.763	-3.0773

## **CHAPTER VII**

**Theoretical prediction of surface  
tension of ternary liquid system  
(nitrogen+oxygen+argon) at  
elevated temperatures and  
different pressures**

## Introduction

Surface tension of multicomponent liquid mixture is useful in the design of separation process as it provides important information about intermolecular interactions in liquid mixtures, and about the structure and energy interactions in the liquid-vapour interface. It is a property of great importance in mass transfer processes such as distillation, extraction or adsorption. It is also useful in environmental engineering and biotechnology considerations. The experimental data of surface tension of multicomponent systems are not always available. Although, measurements have been made for pure components<sup>1-3</sup>. Few measurements are available for the binary but rare on the ternary mixtures. Recently<sup>4-9</sup> surface tension of some multicomponent systems has been measured. So, there is a need to have a simple and reliable method for their prediction. The most frequently used techniques for the prediction of surface tension are Flory-Patterson<sup>10,11</sup>, Volume fraction statistics<sup>12</sup>, Sanchez method<sup>13</sup> and Brock-Bird relation<sup>15</sup>. All these methods, except Brock-Bird relation, need density data.

For the first time, Takami et al<sup>14</sup> measured the surface tension of ternary liquid mixture ( $N_2+O_2+Ar$ ) over a wide range of temperature and pressure, as well as composition. The literature<sup>15-17</sup> survey reveals that such type of data are very rare. Hence, no theory could be applied for predicting the surface tension of such ternary liquid mixtures. The surface tension of liquid nitrogen, oxygen and argon is an important property in designing a distillation column for an oxygen plant.

Here, an effort is made to compute the surface tension of liquid mixtures at elevated temperatures and different pressures using a modified Brock-Bird relation, which needs only critical properties ( $P_c$ ,  $V_c$ , and  $T_c$ ), of the pure components. This modified relation for which no particular theoretical status is claimed, is set out in the theoretical section of this chapter and tested against the observations made by Takami et al<sup>14</sup>. The computations were made for various compositions between the temperature from 90 to 110 K and vapour pressures upto 865 kPa.

## Theoretical

The generalized relation of Brock-Bird<sup>15</sup> based on modified principle of corresponding state (P C S) is purely empirical and is often used to predict the surface tension with the aid of critical constants. The Brock-Bird relation, applicable for a ternary liquid mixture, can be written as

$$\frac{\sigma}{(P_{c,m}^2 T_{c,m})^{1/3}} = \left( -0.951 + \frac{0.432}{Z_{c,m}} \right) (1 - T_{r,m})^{11/9} \quad (1)$$

where  $P_{c,m}$ ,  $T_{c,m}$ ,  $Z_{c,m}$  and  $T_{r,m}$  are respectively the critical pressure, critical temperature, critical compressibility factor and reduced temperature of a ternary liquid mixture. The values of these parameters are obtained by taking mole-fraction averages<sup>16</sup> as,

$$P_{c,m} = \sum x_i P_{c,i}, \quad V_{c,m} = \sum x_i V_{c,i}, \quad T_{c,m} = \sum x_i T_{c,i},$$

$$Z_{c,m} = \sum x_i Z_{c,i},$$

$$Z_c = \frac{1}{R} \left( \frac{P_c V_c}{T_c} \right) \quad \text{and} \quad T_{r,m} = \frac{T}{T_{c,m}}$$

The temperature dependence of the surface tension for many substances has been shown<sup>17</sup> to be proportional to  $(1 - T_{r,m})^{11/9}$ . The assumption, that this temperature dependence is universal, allows one to predict the values of surface tension using eq (1).

Equation (1) has been modified as

$$\frac{\sigma}{(P_{c,m}^2 T_{c,m})^{1/3}} = \left( -0.951 + \frac{0.432}{Z_{c,m}} \right) \left( 1 - \frac{T_{r,m}}{P_{r,m}} \right)^{\frac{11}{8.33}} \quad (2)$$

where,  $P_{r,m} = P/P_{c,m}$

The above relation holds good for predicting the surface tension values at elevated temperatures and different pressures.

The surface tension  $\sigma$  of a pure liquid can be correlated using the equation<sup>15</sup>

$$\sigma = \sigma_0 (1 - T/T_c)^p \quad (3)$$

The values of the parameters  $\sigma_0$  and  $p$  have been taken from literature<sup>14</sup>, and are reported in table 1.

Equation (3) has been extended for ternary liquid mixture:

$$\sigma_m^r = \sum_{i=1}^3 x_i \sigma_i^r \quad (4)$$

where  $r$  is an adjustable parameter, Takami<sup>14</sup> taken its value as 0.25 and 1 while in present work its value is taken 0.611. On using this value better results are obtained.

## Results and discussion

Presently available information on surface thermodynamics of multicomponent liquid systems is far from complete, but this chapter adds a little to the physics and chemistry of such properties of the multicomponent liquid systems by predicting the values of the surface tension  $\sigma_{cal}$  where comparisons can be made. The computed values are found to be in fairly good agreement with the previous data observed experimentally<sup>14</sup>. It is for the first time that the surface tension, on the basis of newly proposed theoretical method, has been computed for the ternary system ( $N_2 + O_2 + Ar$ ) over a wide range of temperature, pressure and varying compositions. The experimental values of surface tension have been taken from the recent work of Takami et al<sup>14</sup>. The calculated values of surface tension from eq (2) along with the experimental one are reported in column (5) and (6) of table 2. The average

percentage deviation is found to be 3.82% only. Experimental results confirm the validity of present empirical method.

The values of the surface tension  $\sigma_{cal}$  have also been evaluated by relation (4) using pure component data, and are listed in column (8) of table 2. The values of surface tension calculated from eq (4) are in fairly good agreement with the experimental values, and those obtained from eq (2) which again demonstrate the validity of the proposed empirical eq (2). Generally, density data are used to evaluate the surface tension of liquid mixtures. Moreover, new values are excellent than those reported by Takami et al.<sup>14</sup> since the average percentage deviation of the new values is only 3.82%.

Because the surface tension of multicomponent system depends upon the relative temperature and pressure, the  $\sigma_{cal}$  and  $\sigma_{exp}$  of the system taken under the present investigation have been plotted against temperature (T/K) and pressure (P/kPa). It is seen from fig 1 that the effect of T and P on  $\sigma_{cal}$  and  $\sigma_{exp}$  values are more pronounced. To summarize, a method of calculation based on the present approach yields encouraging results for ternary liquid mixtures. Since previous methods cannot be applied in the absence of density data, this method is expected to be useful for calculating the surface tension of a large number of such liquid systems.

## Conclusion

Newly proposed empirical method can be used to predict the surface properties of multicomponent liquid systems. The data obtained, using the present approach, are found to be in excellent agreement with the experimental values. The accuracy of prediction is close to one obtained experimentally. To conclude, we may say that the proposed empirical relation and computational methods adopted here, and the relation used for  $\sigma$  using pure component data, not only have an edge over other available methods in predicting the surface properties but also reasonably well suited for carrying out numerical study of the surface properties of multicomponent liquid systems.

The new type of computation method introduced in the present chapter may be physically relevant in evaluating the surface tension of liquid mixtures using critical constant data of pure components. Nevertheless, we believe that this study could act as a guide for developing some more general correlations.

**Table - 1**  
**Parameters used in eq (3)**

Component	$\sigma_0$ (mNm <sup>-1</sup> )	p
nitrogen	28.2	1.235
oxygen	39.5	1.256
argon	38.7	1.299



Table - 2

Surface tension ( $\sigma/\text{Nm}^{-1}$ ) for the  $\text{N}_2$  ( $x_1$ )+ $\text{O}_2$  ( $x_2$ )+Ar ( $x_3$ ) at elevated temperatures (T/K) and different pressures (P/kPa)

T(K)	P(kPa)	$x_1$	$x_2$	$\sigma_{\text{cal}} (\text{Nm}^{-1})$	$\sigma_{\text{exp}} (\text{Nm}^{-1})$	% $\Delta\sigma$	$\sigma_{\text{cal}} (\text{Nm}^{-1})$
				Eq (1)	(ref 8)		Eq (4)
90.1	262.0	0.080	0.505	8.61	8.61	0.03	8.60
92.3	303.0	0.077	0.507	8.48	7.97	6.39	8.52
93.5	311.8	0.076	0.509	8.46	8.52	0.66	8.51
93.9	342.9	0.073	0.511	8.35	8.30	0.64	8.44
94.2	355.0	0.154	0.583	8.05	7.76	3.71	8.30
94.4	337.6	0.156	0.586	8.12	8.27	1.87	8.34
94.6	380.1	0.142	0.595	8.00	7.85	1.92	8.26
94.7	335.5	0.133	0.602	8.22	8.03	2.32	8.39
94.8	362.9	0.134	0.602	8.10	8.02	1.05	8.32
94.8	346.9	0.143	0.592	8.13	8.14	0.10	8.34
95.0	373.7	0.142	0.593	8.03	7.51	6.95	8.28
95.0	351.8	0.138	0.596	8.13	8.23	1.16	8.34
95.1	350.4	0.104	0.624	8.28	8.04	2.93	8.40
95.6	372.9	0.096	0.568	8.48	8.07	5.05	8.35
95.7	365.2	0.117	0.549	8.23	7.87	4.62	8.35
95.9	379.7	0.088	0.577	8.43	8.11	3.92	8.37
96.0	371.5	0.090	0.588	8.36	7.96	4.99	8.37
96.3	322.0	0.147	0.675	7.82	8.45	7.50	8.42

96.4	331.5	0.146	0.677	8.27	8.63	4.12	8.41
96.7	341.4	0.147	0.670	8.77	8.56	2.49	8.35
96.7	384.6	0.146	0.670	8.20	8.16	0.49	8.27
97.0	391.2	0.165	0.672	8.34	7.92	5.25	8.24
97.5	351.0	0.150	0.684	7.97	8.58	7.15	8.35
97.5	478.0	0.146	0.689	7.89	7.40	6.61	8.07
97.7	404.7	0.170	0.656	8.05	8.12	0.92	8.19
97.7	448.9	0.156	0.670	7.88	7.94	0.74	8.12
97.8	428.3	0.103	0.713	7.77	7.89	1.56	8.17
97.9	409.4	0.116	0.700	8.05	7.95	1.28	8.28
97.9	453.1	0.109	0.708	8.07	8.04	0.42	8.20
98.0	461.2	0.102	0.716	8.00	7.76	3.05	8.19
98.2	417.2	0.103	0.715	8.13	7.93	2.49	8.29
98.4	391.5	0.096	0.722	8.27	8.62	4.04	8.38
98.4	419.5	0.096	0.722	8.23	7.91	4.09	8.30
98.6	501.8	0.186	0.781	7.53	7.09	6.19	7.98
98.6	399.4	0.178	0.788	7.94	8.23	3.50	8.22
98.7	440.5	0.181	0.785	7.77	8.12	4.25	8.12
98.7	394.4	0.178	0.788	7.96	8.37	4.87	8.24
98.8	432.5	0.171	0.796	7.85	7.95	1.27	8.18
99.2	412.3	0.130	0.831	7.94	8.44	5.87	8.25
99.6	465.3	0.107	0.852	7.99	7.88	1.44	8.20
100.0	495.9	0.099	0.860	7.90	7.77	1.61	8.15
100.2	484.5	0.093	0.866	7.95	7.83	1.54	8.19
100.3	354.4	0.097	0.858	8.48	8.80	3.64	8.45
100.3	452.7	0.070	0.842	8.08	8.25	2.05	7.94

100.4	497.4	0.073	0.884	8.00	7.67	4.32	8.57
100.4	482.4	0.073	0.883	8.07	7.83	3.12	8.22
100.7	370.0	0.073	0.884	8.51	9.10	6.52	8.50
100.9	346.4	0.069	0.886	8.60	9.28	7.31	8.54
101.1	379.9	0.068	0.889	8.49	9.19	7.61	8.50
101.8	617.2	0.315	0.411	6.58	6.77	2.77	7.46
102.0	501.0	0.330	0.401	6.98	7.31	4.54	7.75
103.1	642.9	0.267	0.392	6.70	6.32	5.96	7.53
103.3	656.9	0.269	0.390	6.66	6.56	1.52	7.49
103.5	530.4	0.264	0.391	7.10	7.61	6.75	7.76
104.2	599.0	0.400	0.532	6.46	6.98	7.41	7.45
104.6	707.1	0.355	0.499	6.28	6.20	1.32	7.28
104.7	580.0	0.359	0.495	6.71	7.25	7.45	7.56
104.9	734.9	0.357	0.496	6.21	6.01	3.27	7.21
105.9	635.7	0.292	0.661	6.80	6.88	1.09	7.57
106.0	550.5	0.265	0.688	7.19	7.75	7.22	7.81
106.1	650.3	0.265	0.690	6.85	6.97	1.68	7.59
106.3	534.0	0.259	0.695	7.27	7.77	6.39	7.86
106.4	563.9	0.263	0.691	7.16	7.56	5.30	7.79
106.6	796.3	0.250	0.704	6.42	6.00	7.07	7.30
106.7	591.8	0.285	0.670	6.99	7.51	6.88	7.69
107.0	518.1	0.190	0.531	7.50	8.08	7.14	7.99
107.0	720.3	0.185	0.536	6.83	6.56	4.12	7.55
107.0	605.1	0.180	0.542	7.24	7.29	0.68	7.81
107.1	593.6	0.181	0.540	7.28	7.56	3.73	7.84
107.3	572.8	0.188	0.533	7.33	7.71	4.96	7.87

107.4	615.9	0.198	0.527	7.15	7.25	1.41	7.77
107.4	603.2	0.196	0.528	7.20	7.54	4.54	7.80
107.6	627.0	0.187	0.535	7.15	7.23	1.07	7.76
107.8	746.0	0.412	0.365	6.04	6.43	6.05	7.13
109.6	809.9	0.452	0.369	5.78	6.09	5.15	6.95
109.8	748.1	0.423	0.382	6.05	6.51	7.03	7.14
110.0	865.0	0.422	0.388	5.70	6.05	5.72	6.89
				APD	3.82		

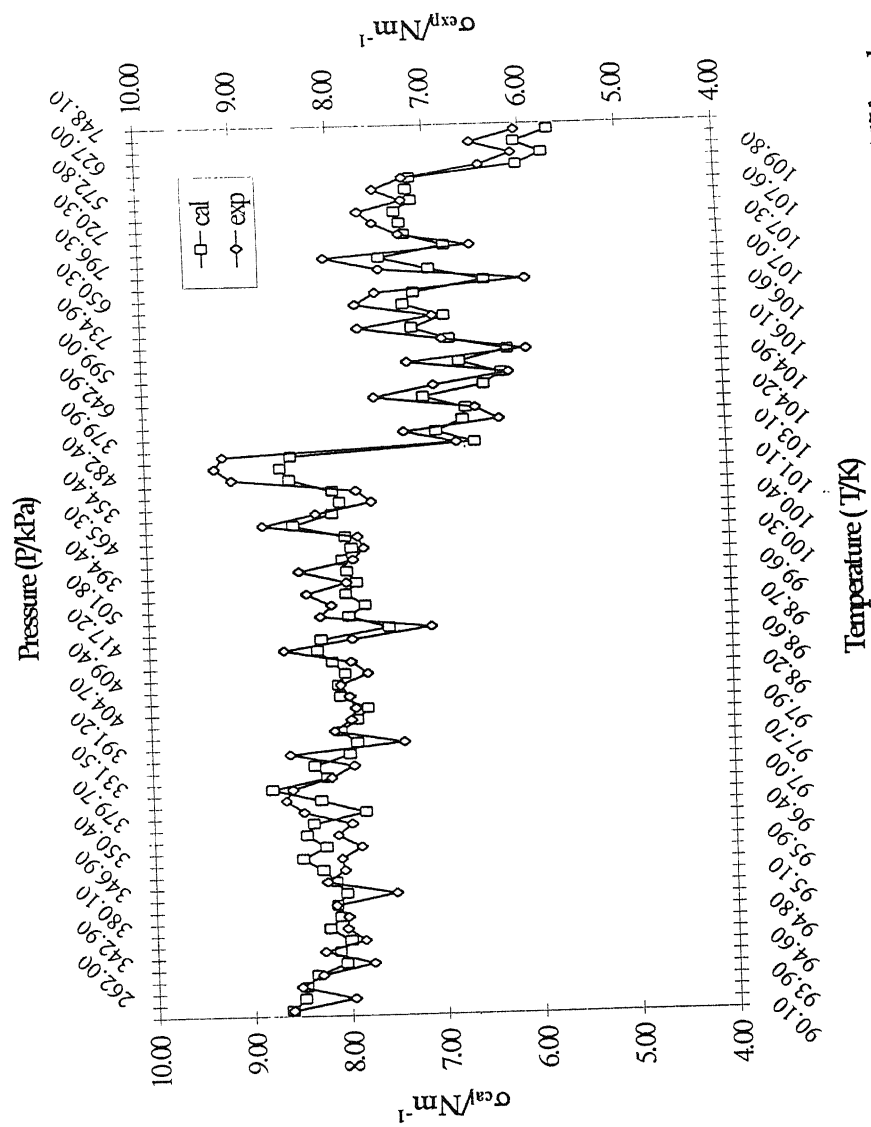


Fig1. Surface tension  $\sigma_{cal}/N\cdot m^{-1}$  and  $\sigma_{exp}/N\cdot m^{-1}$  plotted against elevated temperatures (T/K) and different pressures (P/kPa).

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## **CHAPTER VIII**

**Evaluation of excess surface  
tension of some simple equimolar  
binary mixtures at various  
temperatures and pressures**

## Introduction

A simple hypothesis relating local mole fraction in surface layer of a binary mixture to the density of the system has been proposed by Rowlinson<sup>1</sup>. A relationship has also been proposed to compute surface tension of the liquid mixture from the surface composition of the mixture. Surface tension of the liquid mixture can also be evaluated using the well-established Guggenheim<sup>2</sup> relation from the knowledge of the volumetric and surface properties. Guggenheim's approach has been discussed by Hilderbrand and Scott<sup>3</sup>. Previous workers<sup>4</sup> have utilized Guggenheim relation to estimate the surface tension of liquid mixtures. In the present work, the values of  $g^E/RT$  reported by the Rowlinson<sup>1</sup> have been utilized to deduce surface tension and excess surface tension of some binary mixtures viz.  $N_2+Ar$ ;  $N_2+CO$ ;  $CO+CH_4$ ;  $Ar+CH_4$ ;  $Ar+Kr$ ;  $CH_4+Kr$ ;  $Kr+C_2H_4$ ;  $Kr+C_2H_6$ ; and  $C_2H_4+C_2H_6$  at various temperatures (83.3 to 135 K) and vapour pressure ratio (0.675 to 331). The values of excess surface tension, thus obtained, are compared with the values obtained using Guggenheim relation. The values of excess surface tension, rather than surface tension, are considered for comparative study. The excess surface tension has also been estimated by previous workers<sup>1,5,6</sup>, considering its importance for the study of molecular interaction in liquid mixtures.

## Theoretical

Rowlinson<sup>1</sup> obtained a relation between surface tension and surface composition of the liquid by integrating Gibbs Adsorption equation. The detail of the equation is as follows,

Invariant quantity ( $\Delta\rho_b \Gamma_a - \Delta\rho_a \Gamma_b$ ) can be expressed in terms of  $\rho_a(z)$  and  $\rho_b(z)$  is described here.

$$\Delta\rho_b \Gamma_a - \Delta\rho_a \Gamma_b = \lim_{L \rightarrow \infty} \left( \int_{-L}^L dz [\Delta\rho_b \rho_a(z) - \Delta\rho_a \rho_b(z)] - L [\Delta\rho_b (\rho_a^l + \rho_a^g) - \Delta\rho_a (\rho_b^l + \rho_b^g)] \right) \quad (1)$$

$\rho_a(z)$  can be represented by following relation

$$\Delta\rho\rho_a(z) = y_a\rho^l$$



$\rho_a(z)$  can be represented by following relation

$$\Delta\rho\rho_a(z) = (y_a\rho^l - x_a\rho^g) \rho(z) - (y_a - x_a)[\rho(z)]^2 \quad (2)$$

Similarly the equation for  $\rho_b(z)$  can be written as

$$\Delta\rho\rho_b(z) = (y_b\rho^l - x_b\rho^g) \rho(z) - (y_b - x_b)[\rho(z)]^2 \quad (3)$$

On substituting the values of  $\rho_a(z)$  and  $\rho_b(z)$  from eqs (2) and (3) in eq (1), and solving the equation we get,

$$\Delta\rho_b\Gamma_a - \Delta\rho_a\Gamma_b = \frac{1}{4}(y_a x_b - x_a y_b)(\Delta\rho)^2 \quad (4)$$

where  $t$  is a measure of the thickness of the interface given by the integral

$$t = 4 \int_{-\infty}^{\infty} dz \alpha(z)[1 - \alpha(z)]$$

$\alpha(z)$  can be expressed in classical form by the following expression:

$$\alpha(z) = \frac{1}{2}(1 - \tanh \beta z)$$

The Gibbs adsorption equation in terms of eq (1) and chemical potential  $\mu$  is given by

$$\Delta\rho_a \left( \frac{\partial \sigma}{\partial x_a} \right)_T = (\Delta\rho_b\Gamma_a - \Delta\rho_a\Gamma_b) \left( \frac{\partial \mu_b}{\partial x_a} \right)_T \quad (5)$$

From eqs (4) and (5), we get

$$\Delta\rho_a \left( \frac{\partial \sigma}{\partial x_a} \right)_T = \frac{1}{4} t (\Delta\rho)^2 (y_a x_b - x_a y_b) \left( \frac{\partial \mu_b}{\partial x_a} \right)_T \quad (6)$$

On putting desired quantities ( $x_a$ ,  $y_a$ ,  $y_b$ ,  $g^E/RT$ ) and taking into account necessary assumption from earlier paper<sup>1</sup> in eq (6) and integrating the resulting equation, we get

$$\frac{\sigma_1^{5/3} - \sigma_2^{5/3}}{\sigma_1^{5/3} - \sigma_2^{5/3}} = \frac{(p_1\rho_2 - p_2\rho_1)\ln(p/p_2) + (p - p_2)(\rho_1 - \rho_2) + (g^E/RTp)(p_1 + p_2 - p)(p_1\rho_2 - p_2\rho_1)}{(p_1\rho_2 - p_2\rho_1)\ln(p_1/p_2) + (p_1 - p_2)(\rho_1 - \rho_2)} \quad (7)$$

For the evaluation of surface tension of liquid mixture, with the knowledge of volumetric properties and surface tension of components, Guggenheim<sup>2</sup> proposed the following relation:

$$\sigma_m = \sigma_1 x_1 + \sigma_2 x_2 - \frac{\Sigma}{2RT} (\sigma_1 - \sigma_2)^2 x_1 x_2 \quad (8)$$

where  $\Sigma$  is volume dependent function of surface area of the molecules constituting the system, and  $\sigma_1$  &  $\sigma_2$  are the surface tensions of the pure constituents.

The surface area of the molecule can be approximated using the relation,

$$\Sigma = \frac{\sum_{i=1}^2 V_i^{2/3} N^{1/3}}{2} \quad (9)$$

The excess surface tension of the mixture has been evaluated using the relation

$$\sigma^E = \sigma_m - x_1\sigma_1 - x_2\sigma_2 \quad (10)$$

## Results and Discussion

The values of  $g^E/RT$ , as reported by the Rowlinson<sup>1</sup>, along with the physical properties of pure components at different partial pressures and temperatures, have been utilized to compute surface tension of the binary mixtures. The values of surface tension thus obtained and the values obtained by computing the surface tension from eq (2) have been displayed in table 1. Figure 1 enlists the comparative values of excess surface tension as obtained by Rowlinson's method and Guggenheim relation.

From these results, it is evident that, in all the systems under investigation, the pattern of excess surface tension is the same though there is difference in the individual values of surface tension and excess surface tension. The pattern and sign of the excess surface tension from both methods seem to be the same. As far as the percent difference between the values of surface tension is considered, a fairly good agreement has been achieved in the systems like hydrocarbon mixtures,  $N_2+Ar$ ,  $N_2+CO$ ,  $Ar+CH_4$  and  $CH_4+Kr$ . One of the limitations of the present approach is that the molar volume of the mixture is approximated as to be average of the molar volumes of the individual molar volumes, which is assumed only to be true for purely ideal solutions. Despite of this limitation, fairly good agreement between the values of surface tension and excess surface tension from these two relations has been obtained.

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Table - 1

Surface tension ( $\sigma$ ) and excess surface tension ( $\sigma^E$ )

of the equimolar binary mixtures

Mixture	T	P <sub>1</sub>	P <sub>2</sub>	g <sup>E</sup> /RT	$\sigma_1$	$\sigma_2$	$\sigma_{id}$	Rowlinson		Guggenheim		
								$\sigma$	$\sigma^E$	$\sigma$	$\sigma^E$	%
(1+2)	K	bar	bar		10 <sup>-3</sup>	10 <sup>-3</sup>	10 <sup>-3</sup>	10 <sup>-3</sup>	10 <sup>-3</sup>	10 <sup>-3</sup>	10 <sup>-3</sup>	Dev.
					Nm <sup>-1</sup>	Nm <sup>-1</sup>	Nm <sup>-1</sup>	Nm <sup>-1</sup>	Nm <sup>-1</sup>	Nm <sup>-1</sup>	Nm <sup>-1</sup>	
N <sub>2</sub> +Ar	83.3	1.912	0.689	0.049	7.42	13.39	10.41	9.41	-0.99	9.86	-0.55	4.5
N <sub>2</sub> +CO	83.8	1.912	1.291	0.033	7.42	9.02	8.22	8.03	-0.19	8.18	-0.04	1.8
CO+CH <sub>4</sub>	90.7	2.694	0.117	0.146	7.65	17.78	12.72	9.68	-3.03	11.14	-1.58	13.1
Ar+CH <sub>4</sub>	90.7	1.429	0.117	0.100	11.65	17.78	14.72	13.22	-1.49	14.18	-0.53	6.7
Ar+Kr	120.5	12.660	1.070	0.085	4.98	15.35	10.17	7.98	-2.18	8.9	-1.21	10.9

CH <sub>4</sub> +Kr	116.0	12.410	0.730	(0.05)	12.1	16.27	14.19	13.14	-1.04	13.98	-0.21	6.0
Kr+C <sub>2</sub> H <sub>4</sub>	116.0	0.730	0.008	0.249	16.33	25.72	21.03	17.63	-3.39	19.91	-1.11	11.5
	120.0	1.042	0.014	0.238	15.48	24.96	20.22	16.85	-3.37	19.12	-1.10	11.8
	124.0	1.407	0.022	0.228	14.46	24.2	19.33	15.97	-3.36	18.20	-1.13	12.2
Kr+C <sub>2</sub> H <sub>6</sub>	116.0	0.730	0.002	0.083	16.33	27.36	21.85	18.02	-3.83	20.26	-1.59	11.1
	120.0	1.042	0.004	0.081	15.48	26.69	21.09	17.25	-3.83	19.49	-1.60	11.5
	124.0	1.407	0.006	0.079	14.62	26.07	20.35	16.52	-3.83	18.72	-1.62	11.8
C <sub>2</sub> H <sub>4</sub> +C <sub>2</sub> H <sub>6</sub>	117.0	0.011	0.003	0.129	25.53	27.19	26.36	25.98	-0.38	26.32	-0.04	1.3
	126.0	0.028	0.008	0.114	23.83	25.69	24.76	24.36	-0.40	24.71	-0.05	1.4
	135.0	0.074	0.022	0.102	22.12	24.18	23.15	22.73	-0.42	23.10	-0.05	1.6

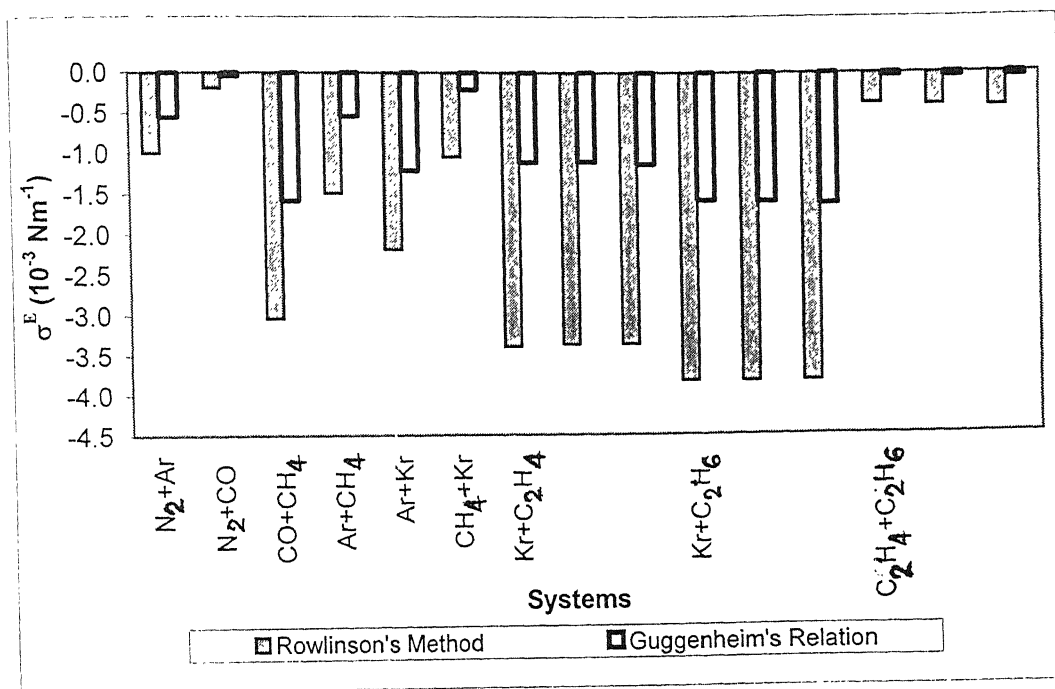


Fig. 1: Comparison of excess surface tension from two methods

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